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CALIFORNIA INSTITUTE OF TECHNOLOGY

POLYMER SCIENCE REPORT

A CROSS-LINKED POLYMER STANDARD
REPORT ON POLYMER SELECTION

W. G. Knauss

AFRPL-TR-65-111   APRIL 1965

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PREFACE

During the past year, the California Institute of Technology has been investigating certain aspects of structural integrity evaluation for solid propellant rocket motors with the support of the U. S. Air Force Rocket Propulsion Laboratory, Dr. F. N. Kelley, Project Scientist. There are presently three parts to the program, each the responsibility of an Associate Investigator as follows:

1. Physicomechanical Behavior of Rubberlike Materials, Dr. P. J. Blatz,

2. Development of a Cross-Linked Polymer Standard, Dr. W. G. Knauss,

3. Solid Rocket Structural Integrity ABSTRACTS, Dr. R. A. Westmann.

The annual report is therefore being issued in parts, consistent with the above division (MATSCIT PS 65-2, AFRPL-TR-65-112, and MATSCIT PS 63-3, AFRPL-TR-65-111, respectively). No summary report has been presented for the third area, except to state that quarterly abstracts were issued beginning in July 1964. Aside from abstracts of pertinent references relating primarily to solid mechanics and material characterization, they have contained guest summary articles by C. H. Parr on Numerical Analysis Methods, by R. F. Landel on Rupture Phenomena, and H. H. Hilton on Viscoelastic Stress Analysis, which surveys were arranged by Dr. A. R. Zak, the first Editor.

This particular report pertains to statements concerning the desirability of a cross-linked polymer standard material, and some of the many technical and administrative problems which must be attacked by the interested collaborators at various laboratories and research organizations.

M. L. Williams

Project Director

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INTRODUCTION

In recent years considerable progress has been made in analyzing viscoelastic structures. While in most instances a viscoelastic analysis is at least in principle not more difficult than a purely elastic stress analysis, it is nevertheless more involved and time consuming – hence, more costly. This fact is easily realized when one considers the material properties determination which consists no longer in measuring a few material constants as for example, when the engineering structural components are made of metals, but require determination of distribution functions in place of the constants.

Because of the increasing importance of polymers in all phases of present day technology, many investigators are working on various aspects of viscoelastic material characterization and on analyses of viscoelastic structures. However, the correlation of their work is often limited to qualitative rather than quantitative comparison and to complementary results. One reason for this relatively poor coordination of research results is the lack of a suitable and commonly available viscoelastic material. Researchers, therefore, usually select for their work a material which is most easily available to them and which satisfies their immediate needs. As a further consequence of such a short-range material selection one finds that available results of analyses in viscoelasticity are not readily incorporated in further work, as the material on which earlier investigation were based is no longer available, and thus considerable data may have to be regenerated. One way of overcoming such difficulties is the development of a suitable, well characterized viscoelastic standard material which is readily available for experimental studies.

This need has been recognized for some time by several researchers. The first program of material standardization was carried out by the National Bureau of Standards with the distribution of the NBS - polyisobutylene. Unfortunately, uncross-linked polymers are not suitable for many aspects of viscoelastic engineering applications, but it is evident that the NBS-PIB standard was largely responsible for the efficient development of a viscoelastic material analysis, both from the standpoint of engineering developments and physiochemical understanding. Similarly, it is anticipated that the evolution of a cross-linked material standard will significantly further the development and improvement of methods in viscoelastic stress analysis relating to cross-linked polymers.

While we have stressed so far the needs facing the stress analysts who are concerned with viscoelastic materials a similar problem confronts those involved in relating the microstructure of polymers to their bulk properties. However, in this case, the requirements on a standard material are more diversified, because in dealing with microstructural variations, the physical chemist must consider a family of polymer systems within which he can study parameter variations. Although such a polymer family could be chosen independently from the requirements of the stress analyst, it appears beneficial to combine these efforts. Thus, a substantial amount of diversified data could be made available on one family of polymers. One would hope that such data relating to the various disciplines of polymer research could aid substantially in furthering the understanding of polymer behavior. Again, it is worth pointing out the important contribution of the NBS-PIB standard to this type of cross-fertilizing endeavor.

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PROGRAM REVIEW

Because one of the objectives of this program is to provide a cross-linked polymer for use in the many phases of polymer research it follows that the ideal material would satisfy the diversified needs of the various disciplines of polymer research. However, the practical situation is such that no single polymer can be expected to be compatible with the full spectrum of investigations on cross-linked polymers. As a compromise it would appear reasonable to select a few polymers which together span a much wider range of material properties than a single polymer can, while avoiding the disadvantages of choosing many diversified standard materials.

In discussions on procedures of polymer selection[*] a number of tentative requirements were established for these materials. In order to aid investigations relating to rubber-like behavior of cross-linked polymers one of these materials should have a low glass transition temperature, say near $-70^{\circ}C$. The low glass transition temperature would permit most studies to be carried out at atmospheric temperatures without special conditioning equipment. For studies of relaxation phenomena and for use in experimental viscoelastic stress analysis investigations one would select a material with a proportionately higher glass transition temperature, say near 10 or $20^{\circ}C$. Because polymer properties are very temperature sensitive near the glass transition temperature, it would be necessary for careful work to use temperature conditioning equipment. However, the temperature in such equipment is usually more easily stabilized near room temperature than at much lower or higher levels. Furthermore, for many

qualitative investigations such as checking experimental arrangements temperature control may not be needed. Thus, considerable advantages for experimental work would result from the choice of such a polymer.

In addition to these general requirements more definite requirements can be set up, although at this early stage they must be viewed as being tentative. The following properties appear to be desirable in any standard polymer considered under this program.

1) Stress optical sensitivity for experimental stress analysis purposes.

2) Optical clearness.

3) No crystallization.

4) Chemical stability.

5) Simplicity of molecular structure

6) Ease of manufacture.

7) Good reproducibility with reasonable care of preparation.

Of these requirements, the optical clearness may not be self-explanatory. It has been found here at GALCIT that optically clear rubbers have aided considerably in the study of failure initiation because the transparency of specimens permitted the visual observation of initial fracture not easily detectable by other means. Also, when high speed phenomena are recorded with the help of high speed photography, it is often desirable to permit maximum light transmission in order to obtain the clearest record possible with high resolution — low sensitivity film. In addition, it has been found that for some experimental stress analyses a so-called fringe sharpener is desirable which apparatus involves repeated traversal of the light path through the specimen; for significantly colored materials, successively

transversing beams are quickly attenuated thus eliminating a potentially useful tool of experimental stress analysis.

In explanation of item 3, it should be clarified that crystallization effects at large strains or low temperatures induce difficulties which at this time unduly complicate polymer mechanical analyses. For this reason the standard material should be chosen as a non-crystallizing rubber.

The major difficulty encountered in this program is not the selection but the procurement of potential standard materials. As a consequence only a limited number of materials have been investigated. As a further result comparatively much time has been spent on developing equipment and general capability of dealing with polymers on a basis appropriate for standard-ization work. While normally this work would have been spread over a longer period of time, its more intense development during the initial year will result in more efficient progress in the future.

Besides the cursory screening of polymers for standardization purposes and the more detailed exploration of a possible standard material two problem areas relating to the standard program were investigated. These problems concern

        1)   methods of measuring the mechanical properties, and

        2)   conversion of measured material properties into related property functions.

Both problems are involved in a careful characterization of a standard polymer.

While, in principle, any one of a number of methods can be used to measure the mechanical properties of a polymer, one finds in practice that this is insufficient for an accurate characterization. Indeed, it

appears that several different methods of measurements should be employed, for, only after they are found to give sufficiently close agreement is one certain of the limits of accuracy for the measurements.

An example of a subtle pitfall in properties measurements which illustrates the need for checking measurements by independent methods was given by Heydemann [1] . In earlier work on the determination of Poisson's ratio from dynamic shear and tensile modulus data Koppelmann [2] contended that the Poisson's ratio of polymethylmethacrylate and polyvinylchloride pass through a minimum in the transition region. Because both the dynamic shear and tensile modulus data appeared reasonable and accurate, this somewhat unexpected anomaly was accepted. In a more careful investigation on the shear and tensile properties of these materials Heydemann showed that the minimum value of Poisson's ratio depends on the rate of temperature change during the testing sequence. He also points out, that if insufficient time (less than ten hours) is allowed for molecular equilibration after the temperature has been changed the resulting measured modulus values may be in error by as much as 40 percent. This is an example where the comparison of independent measurements uncovered, if not an error in measurements, though nevertheless an error in the proper evaluation of the test data.

Equipment for various methods of measuring the mechanical properties has been or is being constructed. In addition to an Instron testing facility a free oscillation torsion pendulum is now in operation. At present equipment for measuring the relaxation modulus is being readied for use. Thus, at least three independent methods are available at this time to determine the mechanical properties of viscoelastic materials.

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Comparison of material properties as determined in different test modes usually requires their interconversion. An effort is made therefore to develop accurate numerical schemes for this purpose. Although only a small number of computer programs of this type are required to satisfy the needs of the experimental program, a variety of interconversions is being considered in order to provide simple methods for calculating those characteristic material functions useful in engineering analyses.

Both the different experimental techniques and the conversion calculations have been applied in the study of a trial standard material. While this material, Solithane 113*, promises to be a versatile polymer with excellent birefrigence properties it possesses some less desirable qualities, the severity of which is being investigated.

In concluding this general review of the program one may notice that, although some rudimentary reference has been made to the chemical behavior of polymers, the initial efforts are strongly oriented towards the mechanical and optical properties of cross-linked polymers. While this bias is not entirely the result of voluntary planning, it was not felt as a serious impediment to the development of the program, because very many of the initial decisions on polymer selection can be made on this basis. Nevertheless, it is expected that during the coming year the chemistry related aspects of this polymer standard program will attract significantly more attention. From an overall viewpoint neither the chemical nor the physical aspects of polymer science should be neglected, nor for that matter, those aspects which have a direct bearing on the engineering analysis of viscoelastic structures.

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* Produced by the Thiokol Chemical Corporation.

SELECTION AND SYNTHESIS OF STANDARD POLYMERS

Because polymers are useful in a large variety of applications
the chemical industry has developed a host of polymer types. One would
normally expect that among these there is at least a small number of
materials suitable for standardization purposes. It is therefore natural
to screen a number of cross-linked polymers for their potentials as
standard materials.

On the other hand one might take the stand that in spite of the
numbers of polymers available, a screening process is relatively
ineffective and costly. Instead one might try the approach of developing a
suitable polymer from first physio-chemical principles. Of course, neither
approach promises success a priori, and, hence, both are being pursued.
While to this time more emphasis has been placed on the screening of
existing polymer systems, there are many reasons for devoting proportionately
more time to polymer synthesis. Future efforts shall therefore be increasingly
concerned with this possibility of polymer evolution.

For the purpose of polymer selection from existing formulations a
list of possible choices was prepared during one of the group discussions at
GALCIT. These materials are shown in Table I. From this initial compilation
a limited number of polymers were chosen for closer investigation. They are
listed in Table II. Because relatively little quantitative knowledge exists on
the birefringence of polymers and because this property is considered an
important attribute of a standard material, first screenings were performed
on this basis: a comparison of the strain-optic properties of Solithane 113,
butylmethacrylate and ethylene-propylene rubber (EPR)* is shown in Figure 1.

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* We are indebited to Dr. W. Bartoe of the Rohm and Haas Company for
supplying the butylmethacrylate and to Mr. J. Maurer of the Enjay Company
for supplying the ethylene-propylene rubber.

INITIAL LIST OF POLYMER STANDARD MATERIALS

TABLE 1

#	NAME	AVAILABLE	Tg°C approx.	OPTICAL PROPERTIES	REPRODUCIBIL-ITY	MODE OF PREP. 2)	CHEMICAL STABILITY before cure3)	after cure	SWELLING equil.	X	SOL-fraction	STRUCTURE KNOWN chem	phys	STRUCTURE phys	HOME GENEITY	DATA AVAIL-ABLE	E LONG MAX.	EASE OF STRUCTURAL VARIABILITY
1	SBR	PHILLIPS(++)	-70	CLEAR WITHOUT ANTIOXIDANT	+	m	A +	+	++	MEAS-URED	10%	+	NON-CRYST.		MUCH DATA++		
2	X-15 (PDB)	PHILLIPS(++)	-70	CLEAR 1) Cs LIKE #8	+	m	A +	+	++	✓	LOW	++	NON-CRYST.		++		
3	X-30 LIKE SBR	?	-70	LIKE #1	+	m	A +	+	++	✓	LOW	++	NON-CRYST.		++		CROSS LINK DENSITY IS EASY TO VARY BY A FACTOR OF 10³
4	PIP	SHELL(++)	-70	CLEAR Cs; MAGNIT.?	+	m	A +	++	++	✓	LOW	++	NON-CRYST		++		
5	EPR	HERCULES DUPONT	-65	Cs LOW?	+	m	A +	++	++	✓	LOW	+	CRYST.				
6	BR	ESSO	-70	Cs LOW?	+	m	+	++	++	✓	LOW	+	CRYST.				
7	PPG-TDT-TMP.	DOW WYANDOTTE DUPONT	-70→+70	CLEAR Cs < Cs #8	O	c	+	-	O	✓	VARIABLE HIGH	O	NON-CRYST.	-	MECH.& OPTICAL DATA ++		FAMILY OF MAT's ADD DPG
8	SOLITHA-NE	THIOKOL	-70→	CLEAR Cs; MAGNIT.?	O	PRE-POLYN C	+	-	O	✓	VARIABLE HIGH	-	NON-CRYST.	-	MECH.& OPTICAL DATA ++		CROSS LINK DENSITY EASY TO VARY
9	BUTYL-METHA-CRYLATE (EDGMA)	ROHM & HAAS (+++)	0→100	CLEAR Cs STRONGLY TIME DEPEND-ENT	++?	START FROM MONOM-ER & C shrink problem	+	++	++	✓	LOW	++	NON-CRYST.		+		FAMILY WITH MMA COPOLYMER
10	BA ZnO	ROHM & HAAS	-40	CLOUDY Cs; MAGNIT?	-;?	m	+	+	-	✓	LOW	O	NON-CRYST	-			
11	PYA (EDGMA)	UNION CARBIDE	+35	CLEAR Cs	+ O	c	+	+	++	✓	LOW	+	NON-CRYST		+		FAMILY
12	BUTAREZ-CTL	PHILLIPS THIOKOL AM SYNTHE-TIC	-87	RED Cs LOW	SOURCE PROBLEM O	c		O?	O?	✓	VARIABLE	-	NON-CRYST	-	+		CROSS LINK DENSITY BETWEEN 11,000-90,000

GRADING SCALE : ++ EXCELLENT / + GOOD / O DUBIOUS / - POOR

NOTES: 1) C_s ~ STRESS OPTICALLY SENSITIVE 2) m = MOLDING C = CASTING 3) A = MAY REQUIRE SPECIAL STORAGE ANTIOXIDANT NEEDED

TABLE II

LIST OF POLYMERS SELECTED FOR INVESTIGATION

ITEM NO.	NAME OF POLYMER	IMPORTANT PROPERTIES
1	Solithane 113	Variable T_g .
2	Butyl Methacrylate	$T_g = + 22^{o}C.$
3	Ethyl Acrylate	$T_g = - 20^{o}C.$ Chemically stable, attractive chemical system.
4	Copolymer of Ethyl Acrylate and Styrene	T_g variable; Improved optical properties over ethyl acrylate.
5	Solprene X-15	$T_g = - 70^{o}C.$ Clear, stress-optic response may be acceptable.
6	EPR	$T_g = - 70^{o}F.$ Chemical stability good.

Whereas Solithane 113 shows a birefringence response which is sufficient for experimental stress analysis work, EPR offers marginal response qualities and butylmethacrylate is not acceptable on this basis. Because the molecular structure of ethylacrylate is not vastly different from that of butylmethacrylate, it was not expected to be substantially different in its birefringence response and was therefore not examined. Similarly the copolymer of ethylacrylate and styrene* was not tested for birefringence behavior because the polymer turned out to be translucent and only transparent to infra red light.

In addition to the polymers of Table II three others have been suggested for consideration. These polymers are:

1) philprene, an SBR rubber produced through butyl-lithium polymerization by the Phillips Company,

2) a castable rubber produced by the Dow Chemical Company which is cross-linked with polypropylene glycol and terminated,

3) a butadiene rubber, Telagen CT, produced by the General Tire Company.

Of these the Dow rubber has been cast. The major difficulties encountered were its tenacious adherence to the polished mold surfaces and its dark red-brown coloration. Ingredients for Telagen CT have just been received but not yet processed.

While the results obtained so far are certainly not numerous the experience with this limited number of tests, together with other investigations [3, 4] tends to emphasize the fact that

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* This copolymer of 45% ethylacrylate and 50% styrene was also kindly prepared by Dr. W. Bartoe of the Rohm and Haas Company.

1) Solithane 113 and other polyurethanes offer high stress-optic sensitivity, but their molecular structure is not simple.

2) The polymers which possess a simple molecular structure are stress-optically not very sensitive.

One is tempted to deduce from these observations that the dual requirement of high birefringence under stress and structural simplicity for one polymer may be hard to satisfy. However, the fact that styrene does not seem to substantiate these two observations, leaves hope that such a polymer can be found. Nevertheless, the establishment of such a standard material may have to be achieved through polymer synthesis.

Efforts in tayloring the properties of polymers to the specific needs of the standard program are still rather limited. Only the simplest method has been tried, namely the "mixing" of polymers to produce copolymers which combine to various degrees the properties of the ingredients. One example was the copolymer of ethylacrylate and styrene mentioned above. It was hoped to combine in this copolymer the birefringence behavior of styrene and the combination of a low glass temperature of ethylacrylate (-20°C) with the high glass temperature of styrene (100°C) to arrive at a stress-optically sensitive material with a glass transition temperature near $+20^{\circ}$C.

Two other copolymers were prepared* of which one was a benzoyl peroxide cross-linked polyester (Paraplex P-13) and the other contained also some styrene. These materials are clear and not rubber like at room temperature. Although no precise measurements have been made

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they appear to have glass transition temperatures near 25°C and 35°C, respectively. Their strain optic coefficients are apparently not very different and are probably in the range from 20 to 60 fringes per unit strain although this response is not very promising it is intended to examine these materials closer.

EVALUATION OF A TRIAL STANDARD

While the cursory screening procedure may eliminate a large number of potential materials from further consideration those which pass the initial selection barriers need to be examined in more detail. However, there exists still the possibility that the detailed investigation points up a major shortcoming which would make this particular material unsuitable for standardization purposes in spite of other favorable properties.

One such potential standard polymer is the urethane Solithane 113*. There are several reasons to consider this polymer as a trial standard. First, this material exhibits excellent optical properties. Second, its mechanical and optical properties can be changed easily and significantly by changing the recipe. Third, it has been used successfully for a number of problems in viscoelastic stress and stress-optic analyses. Fourth, production facilities are available at the California Institute of Technology. Fifth, the characterization of this "guinea pig material" would permit the improvement of experimental methods for characterizing future standard polymers. Its main disadvantages are that it should be stored in a dry atmosphere and that its molecular structure is not particularly simple.

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* Produced by the Thiokol Chemical Corporation, Trenton, New Jersey.

Solithane 113 is marketed as a prepolymer, which may be mixed with several catalysts to produce rubbers which vary at normal atmospheric temperatures from soft to very hard. In this study only one particular catalyst (Thiokol C 113-300) was used. One advantage of starting from a prepolymer instead of a monomer is the small amount of cure shrinkage of the finished product.

Because the prepolymer is hygroscopic, it is stored for production purposes under a dry nitrogen atmosphere in a glass jar within the casting apparatus (cf Figure 2). Another glass jar contains the catalyst. These containers are immersed in a temperature bath which is kept at 60°C during the casting operation to lower the viscosity of the prepolymer for processing. Using dry nitrogen as a pressurizing medium the polymer and catalyst are forced into separate burets, the feed lines and burettes being also immersed in a 60°C water bath. In the burets the components are degassed for 30 minutes under vacuum. This caution ensures removal of gas bubbles and dissolved gases which might influence the cure reaction. Following the degassing procedure the desired amounts of prepolymer and catalyst are forced into a flask immersed in boiling water where they are mixed for at least three minutes with a motor driven stirrer under a dry nitrogen atmosphere. For substantially shorter mixing times non-uniform properties resulted in the final product. * Following mixing, the liquid is fed again under dry nitrogen pressure into a mold preheated to 140°C and cured at that temperature for two hours. A schematic drawing of the production process is shown in Figure 3. A typical mold with polished aluminum surfaces is shown in Figure 4.

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* For a mixing time of two to three minutes, the small strain modulus and the volume change in benzene were measured to be constant within a data scatter of ± two percent. No correlation with mixing time or time lapsed between mixing and casting the liquid into the mold was noticed.

One important factor in the choice of a standard polymer is the reproducibility of its properties in different productions. It is therefore mandatory to study the effect of varying the production parameters in order to assess their relative importance. Essentially two different studies were performed in this respect. One was concerned with the change in properties as a result of varying the relative proportions of prepolymer and catalyst, the other study determined the effect of changing the cure time and cure temperature on a single formulation, termed the equivoluminal composition, because it contains equal volumes of prepolymer and catalyst. We proceed now to consider the results of these investigations.

EFFECT OF COMPOSITION

As mentioned above studies on Solithane 113 have only incorporated a single catalyst. The reasons for this limitation were primarily simplicity of processing and data analysis.

In order to study the physical properties as a function of prepolymer-catalyst composition, six sheet specimens were prepared in which the prepolymer content varied nominally between 43 and 60 percent. These samples were cured at 145°C for two hours, then stored over silica gel for two weeks at room temperature.

Four types of measurements were performed on these formulations:

1) Shear modulus as determined with the torsion pendulum,

2) Strain-optic coefficient at a constant tensile strain rate,

3) Uniaxial tensile strength at a constant tensile strain rate, and

4) Volume increase in benzene.

The results of these measurements are shown in Figures 5 through 12.

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The values of the complex modulus represented in Figure 5 and the loss tangent in Figure 6 are given for the respective natural frequency of free oscillation of the torsion pendulum and are not reduced to a common frequency. The periods of oscillation varied between approximately 10 and 30 seconds per cycle. Note from Figure 6 that for prepolymer contents higher than 52 percent the loss tangent increases sharply, thus indicating that formulations in this range begin to exhibit measurable relaxation phenomena at room temperature over time ranges of several seconds.

This fact becomes more obvious when one considers Figures 7 and 8. These graphs present the real part of the complex modulus and the loss tangent for three compositions which span the straight line portion of G' in Figure 5. The measurements were again obtained with the torsion pendulum and with specimens of nominal dimensions 0.1" x 0.5" x 3". The dimensions were measured to within one thousandths of an inch on an optical comparator. Again, no reduction to a common frequency has been performed.

It is clear from these figures that an increase in polymer content results in an increase of the rubbery modulus as well as in a raising of the glass transition temperature.

Inasmuch as we are interested in a stress-optically sensitive polymer which exhibits significant relaxation effects at room temperatures and under moderate rates of loading, a composition with a still higher proportion of prepolymer would be required, but there is every reason to believe that such a polymer can be obtained with this urethane system. Besides the reservations with regard to the molecular structure this would also entail a relatively high rubbery modulus, possibly in the range of 1000 to 1500 psi. Whether this is an undesirable feature will have yet to be determined.

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From the standpoint of birefringence, a polymer having a high rubbery modulus does not appear to have any disadvantages, as both the stress and strain optic coefficients increase with the percentage of prepolymer content. This fact is clear from Figures 9 and 10 which show the dependence of strain and stress-optic response on the prepolymer-catalyst composition at 25°C.

In view of Figure 9 it is worth digressing for a moment and to consider the problem of quality control. This problem arises whenever polymers are produced in small batches. Supposing then that a polymer has been adopted as a standard material, how could it be established simply whether or not the properties of any material sample fall within previously specified limits? For a birefringent material like Solithane 113 a routine test for the strain optic coefficient under standard loading conditions would provide a simple criterion for such a decision. Because the proportion of catalyst and prepolymer is the hardest parameter to control, its variation would introduce the largest variation in polymer properties and is most sensitively measured by the strain-optic coefficient. For instance, a one percent deviation from the 50-50 percent composition would result in an approximately 15 percent change in the strain-optic coefficient. Similarly, the real part of the complex modulus and the loss tangent could be measured in a standardized fashion. Thus the molecular structure could be easily examined by the optical and mechanical responses in standardized tests. Satisfactory agreement with other specified property requirements would then be also reasonably assured. Of course, every polymer system has its own most sensitive production variable and requires appropriately sensitive quality control tests.

Returning to the evaluation of mechanical properties as a function of composition we consider next the failure stress in uniaxial tension. Figure 11 shows the tensile strength (force at break divided by original cross section) as a function of composition. The specimens were die-cut in dumb-bell form from 0.10" thick sheets; because of attendant defects at the edges limited significance is attributed to the absolute values presented there. However, the trend is definitely clear. Again, a small variation in the composition can have a significant effect on the fracture strength of the finished polymer.

Finally, we examine the volume change in benzene. Specimens approximately 1" x 1/8" x 1/8" were immersed for two weeks in two gallons of benzene at approximately 25°C. The volume change was obtained from measurements of dimensional changes before and during submersion with a travelling microscope. No modulus measurements in the swollen state have been made yet, hence, the cross-link density cannot be determined for these formulations. It is expected to make such determinations in the future.

The swelling tests were performed in order to see whether such a test could provide a simple and accurate quality control measurement. However, it is seen from Figure 12 that the data scatter is too large for such a purpose when the volume of prepolymer exceeds 50 percent.

In concluding this section on the effect of prepolymer-catalyst proportioning, it is well to point out again that a composition can probably be found which provides a high birefringence (on the order of one fringe/psi/inch or higher) while exhibiting viscoelastic properties at room temperature (the glass transition temperature near 10°C). Also, material properties are best monitored from a quality control standpoint by measuring the modulus (shear modulus) and strain optic coefficient under standard conditions.

FURTHER INVESTIGATION OF THE EQUIVOLUMINAL COMPOSITION

While a thorough investigation of the Solithane rubber would comprise more detailed examinations of several of the previously described formulations, we have chosen here to investigate only one special formulation in the hope that it is indicative of the properties of other formulations. The composition of 50 percent catalyst and 50 percent prepolymer (by volume) was chosen arbitrarily.

The exploration of this formulation divides into essentially three parts. Because the physical properties of this material will depend on the time and temperature of the curing reaction, their sensitivity to these parameters was investigated. Secondly, measurements of the mechanical properties through the glass transition range have been started, and, thirdly, comparisons of these measurements with those obtained by investigators at other laboratories and by different methods are being made. The latter effort serves already as a small pilot program for the use of a polymer standard inasmuch as the comparisons should render information on the accuracy of the various methods employed.

A Study of Properties Reproducibility

Besides the relative amounts of catalyst and prepolymer there are other factors which influence the physical properties. Among these the cure time and cure temperature and storage conditions have possibly the largest effect.

With regard to storage, only the effect of moisture has been measured in a cursory fashion. After removing the material from the post-cure conditioner* samples of nominal dimensions 5" x 0.75" x 0.1" were

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* It will be recalled that after cure the material is placed over dry silica gel for two weeks.

weighed and then 1) placed over freshly dried silica gel, 2) exposed to
the room atmosphere with an average of 40 percent relative humidity, and
3) placed in water. The observed weight change after ten days is shown in
Table III.

TABLE III

Percent Weight Change of Equivoluminal Composition

SAMPLE EXPOSED TO	PERCENT WEIGHT CHANGE
Dry silica gel	-0.002
Room atmosphere	+0.098
Water	+0.30

The samples were then exposed to a vacuum of one mm H_g for three hours.
The samples exposed to the room atmosphere and to water essentially regained
their initial weight in this time. One would conclude, therefore, that water
absorption is limited to a thin surface layer and probably does not affect the
bulk of the material during relatively short exposure times.

In order to assess the sensitivity of the properties to variations in
the cure time and cure temperature a set of 15 polymer sheets were prepared
according to the scheme in Table IV.

TABLE IV

Cure Time and Temperature for Control Test
on Fifteen Specimens

Cure Temperature °C	Cure Time - Hours				
	$\frac{1}{2}$	$\frac{3}{4}$	1	$1\frac{1}{2}$	2
125	▨		▨		▨
135			▨	▨	
145	▨	▨	▨	▨	▨
155		▨	▨		
165	▨		▨		▨

The results of this parameter study are shown in Figures 13 and 14. Figure 13 depicts the dependence of the modulus properties on cure temperature for various cure times. The measurements were again obtained with the torsion pendulum at 20°C and have not been reduced to a common frequency.

Because this cure parameter study was performed before the sensitivity of the physical properties to small changes in the catalyst-prepolymer, ratio was realized. Thus the scatter in the modulus data is probably due to errors in the formulations. However, it will be recalled from Figure 6 that the loss tangent is insensitive to small deviations from the equivoluminal composition. The loss tangent data should therefore be a meaningful, if not complete, indication of the effect of cure time and temperature on the physical properties. Two observations deserve special mention. First, the mechanical properties do not appear to be as sensitive to variations in cure time and cure temperature as to variations in catalyst-prepolymer composition. Second, the effect of uncontrollable variations in cure time and cure temperature can be minimized by selecting appropriate values for them. This is evident from Figure 14 which represents a contour map of the loss tangent. In principle one could select a cure time and temperature near which the minimum loss tangent occurs because the gradients are small in this vicinity and minor variations will have little effect. On the other hand, when the material is poured into a mold above 145°C curing can occur so fast on the surfaces of the mold that flow patterns of the quickly solidifying liquid are retained in the sheet material. But even within this limitation a region can be found where property gradients are small so that small changes in the mechanical properties result if a small error is made in the cure time or temperatures.

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This analysis is, of course, strictly applicable only to the loss tangent. However, in principle the same type of analysis can be performed for any other property and should be carried out after a material has been chosen as a standard.

Similar to the modulus data the birefringence measurements show too much scatter to make an interpretation meaningful. Interestingly enough, the correlation between the modulus and birefringence data is so good that the composition of the test specimens can be determined rather closely.

In concluding this section on the factors influencing the physical properties of the equivoluminal composition, it should be remembered that different formulations might require much closer control on the production parameters than is indicated by the present results if only small variations in the physical properties can be tolerated. Nevertheless, the type of investigation outlined here should apply to some extent also to other formulations, at least with regard to order of magnitude of error that may be expected if, e.g., the cure time and temperature are changed a small amount. Inasmuch as the present equipment for the production of Solithane 113 allows temperature control to $\pm$ 1°F and timing to three minutes (time required to disassemble the mold) these two parameters do not appear to be a major factor in the batch-to-batch variability of Solithane 113 castings.

The Mechanical Properties in the Transition Range

Because of the limited frequency range of a freely oscillating torsion pendulum the data on the shear modulus in Figures 5 and 6 give primarily information on the temperature dependence of the modulus. In order to deduce from such results the time or frequency dependence of the shear modulus it is necessary to obtain a time-temperature relationship.

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This determination requires independent tests which establish whether 1) the material is thermorheologically simple, and 2) determine the shift factor relationship connecting time and temperature. If the material is not thermorheologically simple the problem is more complicated (see, for instance, References 5, 6).

Since a complete thermomechanical characterization requires additional characterization tests one might ask why measurements with a torsion pendulum are needed inasmuch as they duplicate such tests and give less information. The answer lies in the fact that a single method of material characterization is rarely sufficient to assure accuracy of the results [6] . We refer here again to the previous discussion on the necessity of independent test methods in material characterization and to the example of Heydemann's measurements.

As an example which arises out of the characterization of the Solithane 113 system we present the comparison of the relaxation modulus as obtained earlier from constant strain rate experiments [7] with data derived from torsion pendulum tests. Because the constant strain rate tests were performed before the present study of the catalyst-prepolymer compositions, the material tested, and believed to be the equivoluminal one, may have actually been of slightly different composition because of a presumably small processing error. While this possibility could have been confirmed on the basis of comparing the rubbery modulus, the comparison of the two independent measurements throughout the transition range emphasizes this fact. Figure 15 shows the torsion pendulum data of Figure 7 for the equivoluminal composition plotted as a function of the temperature reduced frequency ωa_T . The shift factor a_T was taken from

the earlier measurements on the relaxation modulus [7] . The same figure

shows the real part of the complex modulus as calculated from that relaxa-

tion modulus. Clearly the difference between the two curves is too system-

atic and too great to be entirely due to faulty measurements. On the

other hand the difference is essentially accounted for if the earlier formula-

tion was actually one containing between 46.6 and 47.6 percent prepolymer

and not 50 percent as was believed.

While then the present comparison did not provide a check on the

accuracy of the measurements, it has demonstrated how an error was

discovered in the material formulation.

Comparative Measurements Performed by Different Investigators

In keeping with the goal of the polymer standard program a small

effort was started to compare measurements made by different investigators

and with different techniques. At this time two companies are participating

in determining the dynamic modulus of the equivoluminal formulation .

At the Atlantic Research Corporation, Alexandria, Virginia, the Fitzgerald-

Ferry transducer is being used in the characterization , while at the Lockheed

Propulsion Company, Redlands, California, a piezzo-electric driving system

is being developed for the dynamic characterization in either the shear or

extension-compression mode*[8].The specimens for these investigations were

cut from the same sheet so that material variability was ruled out.

The data obtained with the Fitzgerald-Ferry transducer is not

sufficiently complete for reporting. On the other hand, the comparison of

the torsion pendulum and LPC piezzo-electric driver has already effected an

* We are indebted to Mr. Courtland Robinson of the Atlantic Research
Corporation and Mr. Dalton Cantey of the Lockheed Propulsion Company
for making their facilities available.

evaluation of the latter's potential. The limited amount of data obtained with the piezzo-electric driver seemed sufficient to deduce a shift factor relation which was then used to determine the real part of the complex modulus as obtained from torsion pendulum measurements. These data are compared in Figure 16. The relatively small disagreement is probably due to the fact that only a limited amount of data was available to deduce the time-temperature shift factor relation.

It is hoped that more comparative measurements of this type can be carried out in the near future.

INTERCONVERSION OF MATERIAL PROPERTIES

To facilitate the conversion the characteristic material functions into associated forms, such as for example, relaxation modulus to dynamic compliance or creep compliance to dynamic modulus, a small library of IBM 7094 computer programs has been started. Essentially two methods of conversion are being employed one resting on the determination and use of the spectral distribution functions, the other on the Prony series representation of the relaxation and creep functions.

While a number of programs are operating properly others have only been started. The major difficulty is encountered in the determination of the relaxation spectrum and the Prony coefficients. In both cases positive and negative values appear but negative values are physically not acceptable. In some applications negative values for some of the Prony coefficients will be quite acceptable. For instance, the relaxation modulus can be represented quite well even though some of the Prony coefficients are negative. However, when the same set of Prony coefficients is used to calculate the complex modulus one finds that the imaginary part is rather

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sensitive to the sign of the coefficients in the series representation. Instead of a smoothly varying function there results one which exhibits oscillatory behavior approximately according to how often the Prony coefficients change sign. Essentially the same difficulty is encountered with the determination of the relaxation spectrum and its use in calculating the various functions. However, the difficulty does not arise because of numerical methods but is mostly the result of not being able to specify the relaxation modulus accurately enough as a function of time.

At this time the programs which operate satisfactorily are:

1) Determination of Prony coefficients from

    a) Relaxation modulus

    b) Constant strain rate master stress-strain curve.

2) Determination of

    a) Relaxation modulus

    b) Complex modulus

    c) Complex compliance

    d) Stress in a constant strain rate test

from either the relaxation spectrum or the Prony coefficients. The program for the determination of the relaxation spectrum from either the relaxation modulus or constant strain rate data is also operating but is not yet fully automatic, in the sense that it requires iterative adjustments based on earlier program outputs until a satisfactory solution is obtained.

During the next year the latter program will be made more efficient and further programs will be developed. It is hoped that a compact package of computer programs can be developed which is easily and effectively used by both engineers and polymer physicists.

CONSTRUCTION OF A TORSION PENDULUM

One of the simplest instruments for the measurements of the mechanical properties of polymers is the free oscillation torsion pendulum. While its simplicity of construction and application is the main advantage over other measuring devices its chief limitation is its narrow frequency range of operation. For this reason the torsion pendulum is commonly employed to obtain information of the temperature dependence of visco-elastic materials rather than the frequency dependence.

Because measurements can be made quite easily once the additional equipment is set up, the torsion pendulum is ideally suited to perform quick and accurate quality control tests on materials produced for standardization purposes. It was originally for this reason that the present simple pendulum was constructed. In order to make use of its potential accuracy in material characterization measurements, it was designed compactly to fit into available temperature conditioning equipment. In this respect it deviates from most torsion penduli which require considerably more space for operation.

DESIGN AND OPERATION

The torsion pendulum is shown in Figure 17 with a specimen in place. While we need not elaborate on the principle of operation, it is of interest to point out some special features.

First, in order to achieve a sufficiently compliant suspension for the torsion bar (cf Figure 17) while keeping the height of the assembly small, a steel strip of cross-sectional dimensions 0.001" x 0.10" was used rather than the commonly employed round wire. For the same load carrying

ability a round wire of the same material would have to be 50 times as long to provide the same low torsional rigidity as the short metal strip. Second, initiation of purely torsional oscillations can present a problem. The support of the suspension strip and lower specimen clamp was therefore mounted on a frame which could be rotated around an axis through the longitudinal axis of the specimen and the suspension strip. Rotating this arrangement quickly through a small angle and bringing it to rest suddenly in a latching arrangement will cause the torsion bar to perform pure rotational oscillations, provided the whole assembly is carefully levelled. For operation from outside of the temperature conditioning chamber the latch may be lifted with a solenoid and the rotation is effected by means of a long bar rigidly connected to the rotating frame. For convenience two Selsyn motors were used to induce rotation.

Finally, the means of recording the motion of the torsion bar deserves mention. Provision has been made for two ways of recording the motion. In one method a multiply wound coil which is rigidly connected to the torsion bar moves in a magnetic field thus generating a voltage proportional to the angular velocity of the torsion bar. The voltage can be recorded on a strip chart recording voltmeter. Because the voltage generated in the coil is proportional to the velocity this method cannot be used for frequencies smaller than 0.001 cycles per second. For smaller frequencies an optical method may be employed, which makes use of the smaller mirror mounted on the torsion bar. A light beam from a stationary source can be reflected by this mirror onto a scale. Because the motion is slow the maximum excursions can be easily determined and together with the frequency, this information is sufficient to calculate the complex modulus.

In measurements at higher frequencies this mirror has provided an added simplification in measuring technique while adding substantially to the accuracy of the measurements. This was accomplished by reflecting a light beam such that it passed a slit behind which a photomultiplier tube recorded a pulse whenever the light beam passed by. By feeding these pulses into an electronic counter the time for several periods of oscillation could be easily measured and read out in digital form to better than one percent accuracy. This was more convenient and more accurate than reducing the strip chart records resulting from the voltage output of the recording coil. The entire set-up is shown diagramatically in Figure 18.

CALIBRATION AND MECHANICAL PROPERTIES CALCULATIONS

The angular motion of the torsion bar is governed by the differential equation (θ = angular displacement)

$$I \frac{d^2\theta}{dt^2} + KG*\theta = 0 \tag{1}$$

where $G*$ may be a complex modulus, I is the moment of inertia of the torsion bar, and K is a function of the specimen dimension only. Assuming a solution of the form

$$\theta = Ae^{i[\omega + i\eta]t} \tag{2}$$

one finds from (1)

$$- I [\omega^2 + 2i\omega\eta - \eta^2] + KG' + KiG'' = 0 \tag{3}$$

or

$$\omega^2 - \eta^2 = \frac{KG'}{I}$$

$$\omega\eta = \frac{KG''}{2I} ; \quad G* = G' + iG''. \tag{4}$$

Here G' and G" represent the combined properties of the specimen and the suspension wire.

In the present case the contribution of the suspension strip may be neglected because its stiffness was several orders of magnitude smaller than that of any specimen tested. According to equation (2) the decay coefficient η may be determined by plotting the maximum values of the angular displacement of velocity against the logarithm of corresponding times and measuring the slope of the resulting straight line relationship. A typical experiment record and corresponding plot to measure η are shown in Figure 19.

Alternately, the logarithmic decrement, defined as the natural logarithm of successive maximum amplitudes, i. e. ,

$$\delta = \ell \mathrm{n} \, A_i / A_{i+1} = 2\pi \, \eta / \omega \tag{5}$$

may be used to determine G' and G". In terms of the logarithmic decrement equations (4) can be written as

$$\omega^2 \left[1 - \left(\frac{\delta}{2\pi} \right)^2 \right] = \frac{KG'}{I}$$

$$\omega^2 \delta = \pi \frac{KG''}{I} \tag{6}$$

from which the loss tangent G"/G' is found as

$$\tan \Delta = \frac{G''}{G'} = \frac{\pi \delta}{1 - (\frac{\delta}{2\pi})^2} \tag{7}$$

Note that if damping is small, i. e. $\frac{\delta}{2\pi} \ll 1$, then

$$\tan \Delta = \pi \delta \tag{8}$$

If the damping is large the motion may be supercritically damped and no oscillation results.

It can be shown that this situation arises if the inequality

$$\frac{4I\omega^2}{K} < \tan\Delta \cdot G''$$ (9)

is satisfied. In view of (6) and (7) the inequality (9) may be rewritten as

$$4 < \frac{\delta^2}{1-\left(\frac{\delta}{2\pi}\right)^2}$$ (10)

from which one finds $\delta > 0.605$ and $\tan\Delta > 1.9$. Thus the free oscillation torsion pendulum cannot be easily used if the loss tangent exceeds 1.9. It may be seen that the maximum values of the loss tangent in Figure 8 are barely larger than 1.9; the excess is probably due to some difficulty in reducing the data for this highly damped oscillation. Furthermore, it follows from these considerations that for a free oscillation torsion pendulum the approximation (8) involves an error which is always smaller than one percent.

The determination of G' and G'' from equations (4) involves the specimen geometry through the factor K and the inertia of the torsion bar I. We shall now consider the errors in the modulus values which arise as a result of variations in the moment of inertia and the specimen dimensions through the geometric factor K.

Inasmuch as the geometry of the torsion bar is not conducive to calculating its moment of inertia, it was determined experimentally. This was done by suspending a simple rod of calculable moment of inertia at its center from a long wire to form a torsion pendulum and measuring the

period of torsional oscillation. Using the same wire (and the same wire length) the frequency for the pendulum torsion bar was measured. The moment of inertia of this torsion bar I_{TB} could then be calculated from the moment of inertia of the reference bar I_R and the corresponding oscillation periods T_{TB} and T_R according to the relation

$$I_{TB} = \left(\frac{T_{TB}}{T_R}\right)^2 I_R \tag{11}$$

Using multiple measurements and appropriately weighed averages the moment of inertia of the torsion bar with weights was determined to be

$$I = 9237 + 3735 \, (y + 0.372)^2 \; gm - cm^2 \pm \frac{1}{2} \; percent \tag{12}$$

where y is the distance of the weights from the center. Actually the error was found to be somewhat smaller than 1/2 percent.

More sizable errors may occur because of uncertainties of the specimen dimensions. The geometry factor K is given for a rectangular cross-section by

$$K = \frac{cd^3 \mu}{16 \, L} \tag{13}$$

where   c is the strip width

                 d its thickness

                 L its length, and

                 μ a shape factor.

The shape factor μ is given as a function of the c/d ratio in Table V*.

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* This table has been taken from Reference 9.

TABLE V

Shape Factor μ as a Function of c/d

c/d	μ	c/d	μ
1.00	2.249	3.50	4.373
1.20	2.658	4.00	4.493
1.40	2.990	4.50	4.586
1.60	3.250	5.00	4.662
1.80	3.479	6.00	4.773
2.00	3.659	7.00	4.853
2.25	3.842	8.00	4.913
2.50	3.990	10.00	4.997
2.75	4.000	20.00	5.165
3.00	4.213	50.00	5.266
		100.00	5.300

Because the percent error in the thickness is probably the largest and in addition is magnified by the third power of the thickness, this quantity probably introduces the dominant error. For a typical specimen of thickness 0.10" and a measurement accuracy of between 0.0005" and 0.001", this error introduces an error of approximately two percent.

Similarly, significant errors may occur if the specimen is not properly inserted into the pendulum. In particular, if a tensile strain is imposed on the specimen, the period of oscillation may be effected. Equation (1) describes the pendulum motion if the specimen is not stressed axially. If an axial stress exists then the error may be estimated by considering the elastic response of a specimen. For the case of a

rectangular specimen Timoshenko [10] shows then that KG* must be replaced by

$$KG^* = KG' \rightarrow KG' \left\{ 1 + (\frac{c}{d})^2 \; \frac{4}{3\mu} \; \frac{\sigma}{G'} \right\} \tag{14}$$

which, for an incompressible material, becomes

$$KG^* \rightarrow KG' \left\{ 1 + 4 (\frac{c}{d})^2 \; \frac{e}{\mu} \right\} \tag{15}$$

the second term in the brackets representing the error due to an axial strain e .

Let us estimate this error for a typical specimen as used in this work (length L = 3 inches, c/d = 5 , μ = 4. 7). If such a specimen were elongated one thousandth of an inch the corresponding error in the modulus would be approximately one-half of a percent. Great care was therefore in order to keep the axial strain small. However, by lowering the width to thickness ratio this error can be virtually eliminated.

In concluding the discussion on the accuracy of measurements with the torsion pendulum, it should be recalled that a number of causes may contribute to errors in the modulus value. A reasonable estimate of the overall accuracy potential for the pendulum would be on the order of five percent. With sufficient care this value can probably be reduced to two or three percent. More accurate measurements will require much more effort in experimental techniques.

CONCLUSIONS

In summarizing the work reviewed here, it is clear that the
mechanical and engineering aspects have been emphasized over chemio-
physical problems of the polymer standard program. While this has been
dictated largely by the development of equipment and analysis methods
appropriate for such a program, future efforts will be oriented equally
toward these two related areas. More specifically, an increasing
proportion of time will be spent in systhesizing suitable polymers. If it
turns out that the screening of existing polymers holds limited promise
for finding acceptable materials, polymer synthesis will be the only useful
path to success.

In view of the past goal to establish a minimum number of standard
polymers and in view of the requirements specified for such cross-linked
polymers, we anticipate the characterization of three polymers.

In order to satisfy the needs of the stress analyst, one material
should be highly stress birefringent and optically clear. For this material
the requirement of a simple molecular structure may be waived if necessary,
but its glass transition temperature should be variable, either by different
simple formulation as in the Solithane 113 system examined here or by
plastication. The range of glass transition temperature should include
$20 - 25^{\circ}C$.

The remaining two materials should possess a relatively simple
molecular structure while exhibiting significant, if not extremely sensitive
stress-optic properties. At the same time these materials should be clear
to aid in work related to the strength of polymers. For both materials it
should be relatively easy to change the cross-link density consistently. One

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of these polymers should have a low glass transition temperature $(-70^\circ C)$ for work relating to the rubbery behavior of polymers, whereas the other one should have a glass transition temperature near room temperature. The possibility of changing the glass transition temperature over a range which includes the specified values would greatly enhance the value of the standard materials. It should also be clear that thermorheologically simple materials are preferable for any of the standard polymers.

The choice of such three materials will provide a useful compromise between the many requirements of polymer research and engineering on the one hand, and the advantage derived from developing a limited number of polymers for standardization purposes, on the other.

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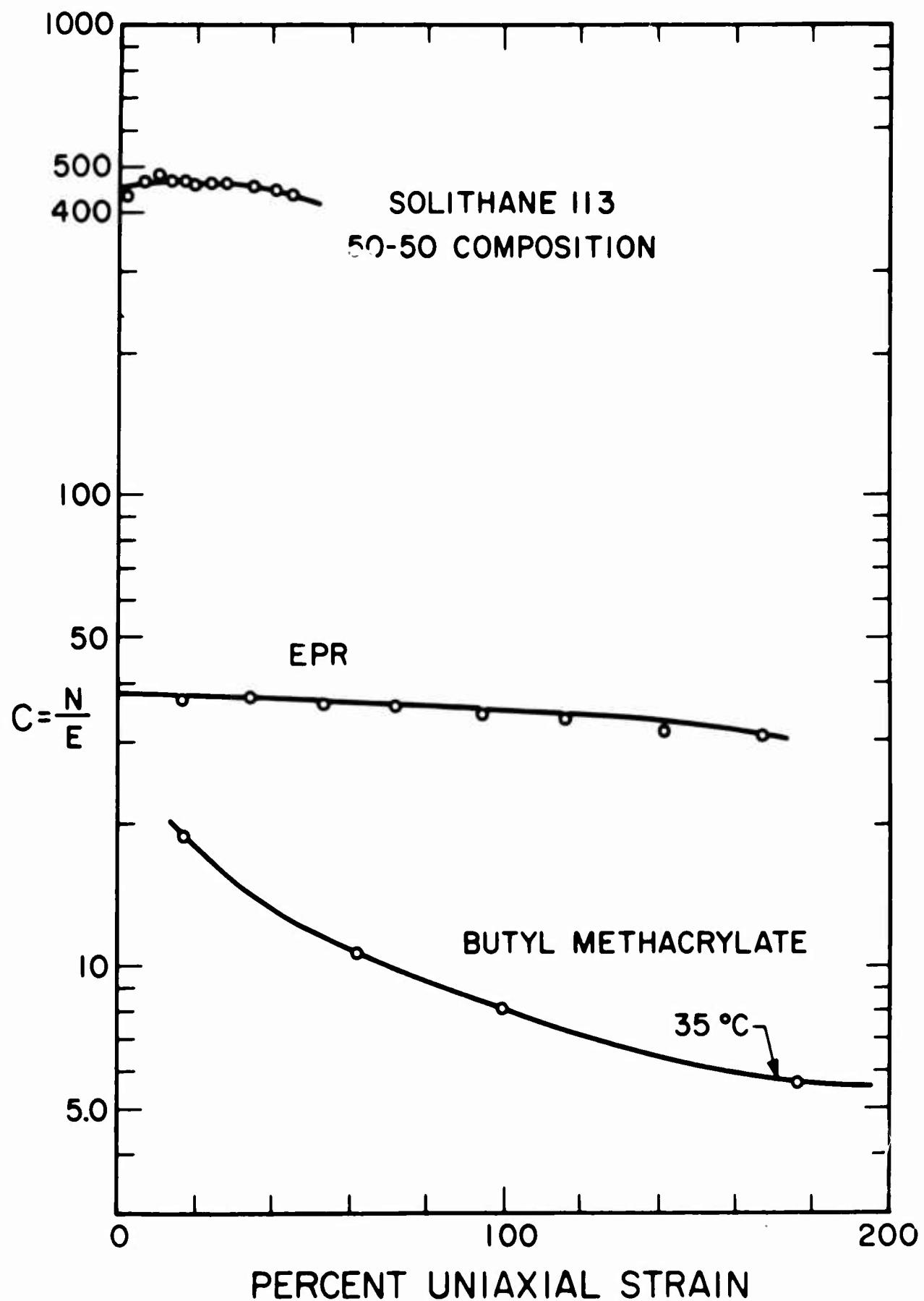
Figure 1. Strain Optic Coefficients (Number of Fringes per Strain per Unit Thickness) as a Function of Strain.

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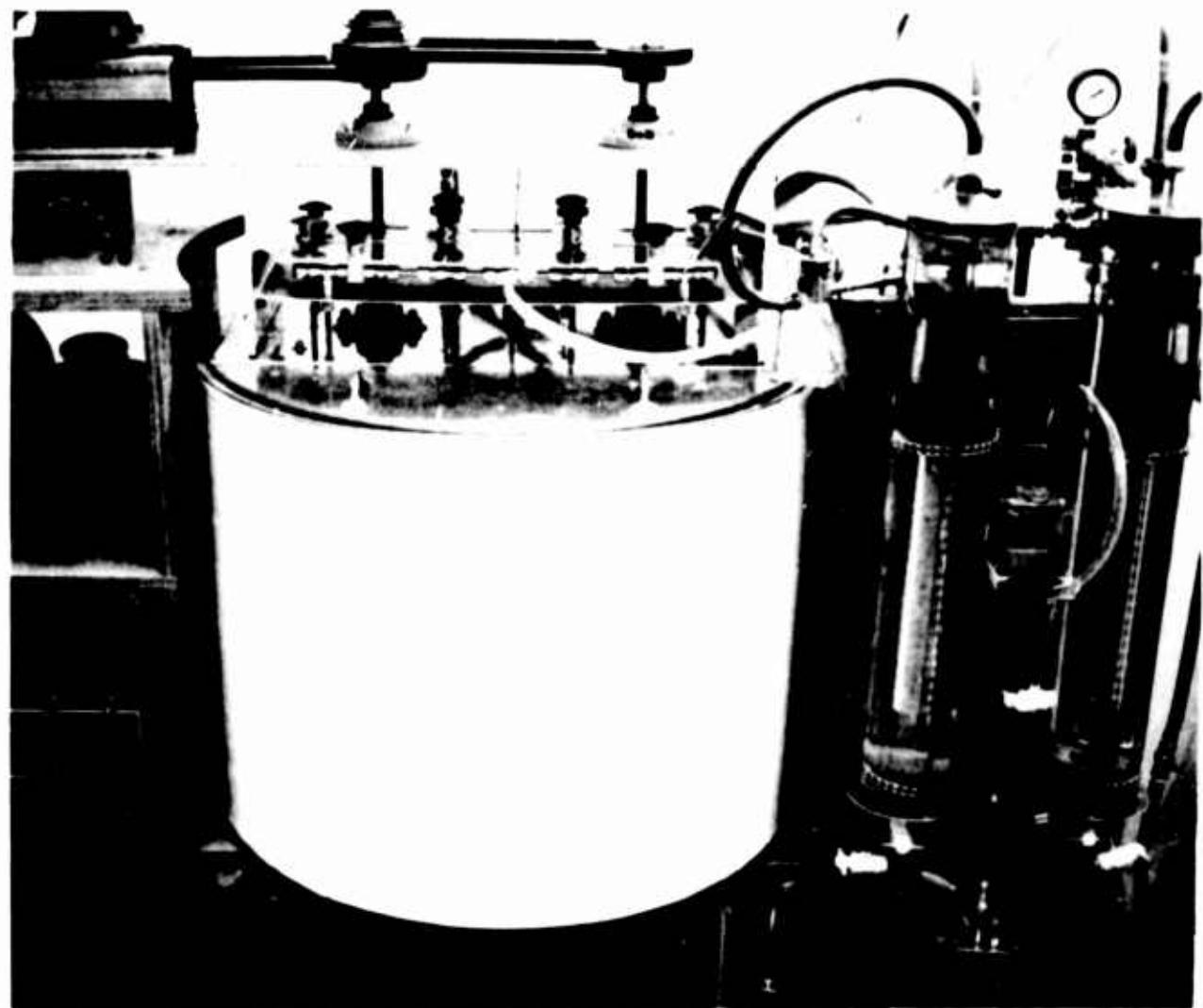
Figure 2. Solithane 113 Casting Facility
(Showing insulated heat bath tank, valving
system and measuring burets).
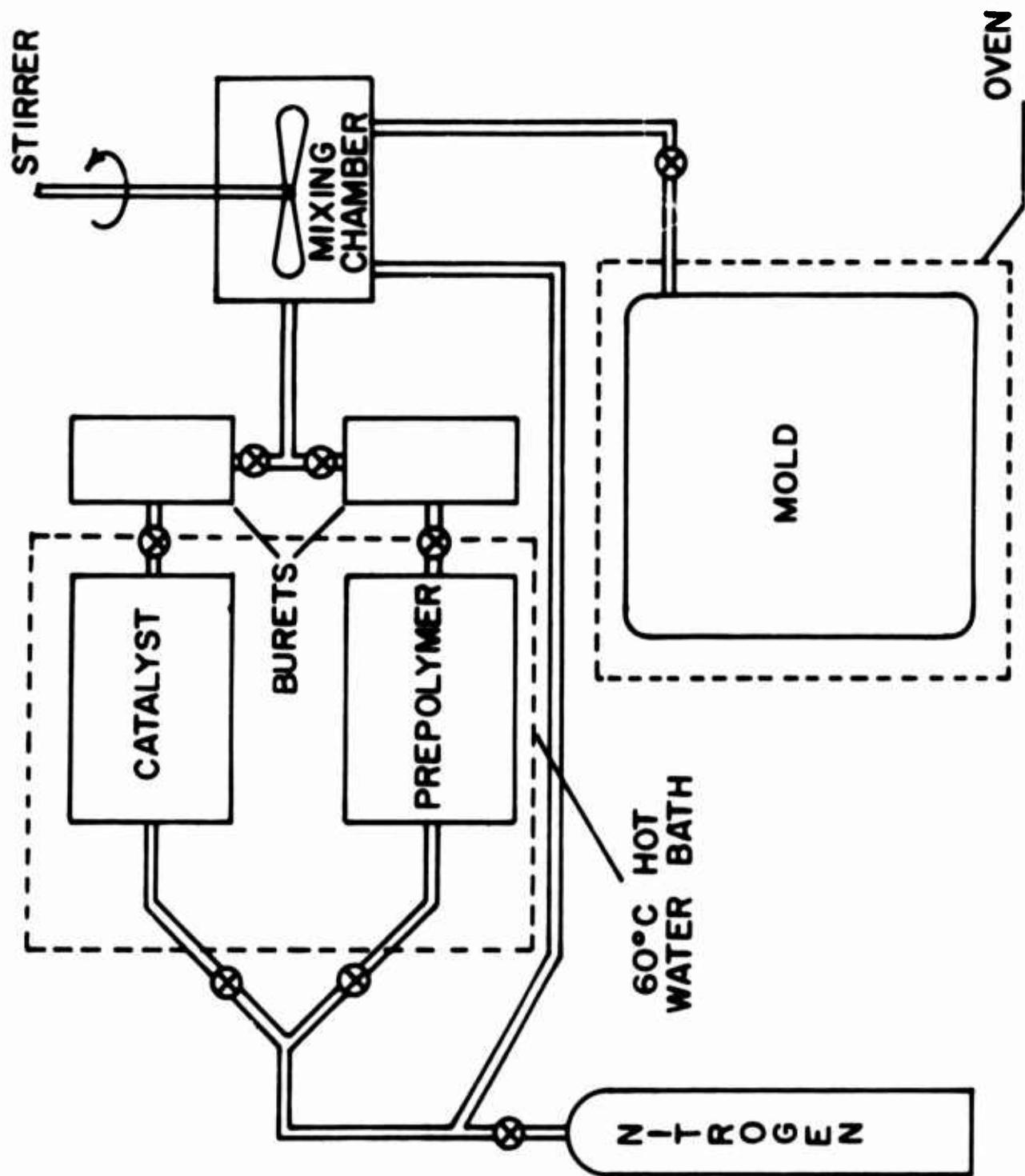
Figure 3. Schematic of Solithane 113 Production Facility.
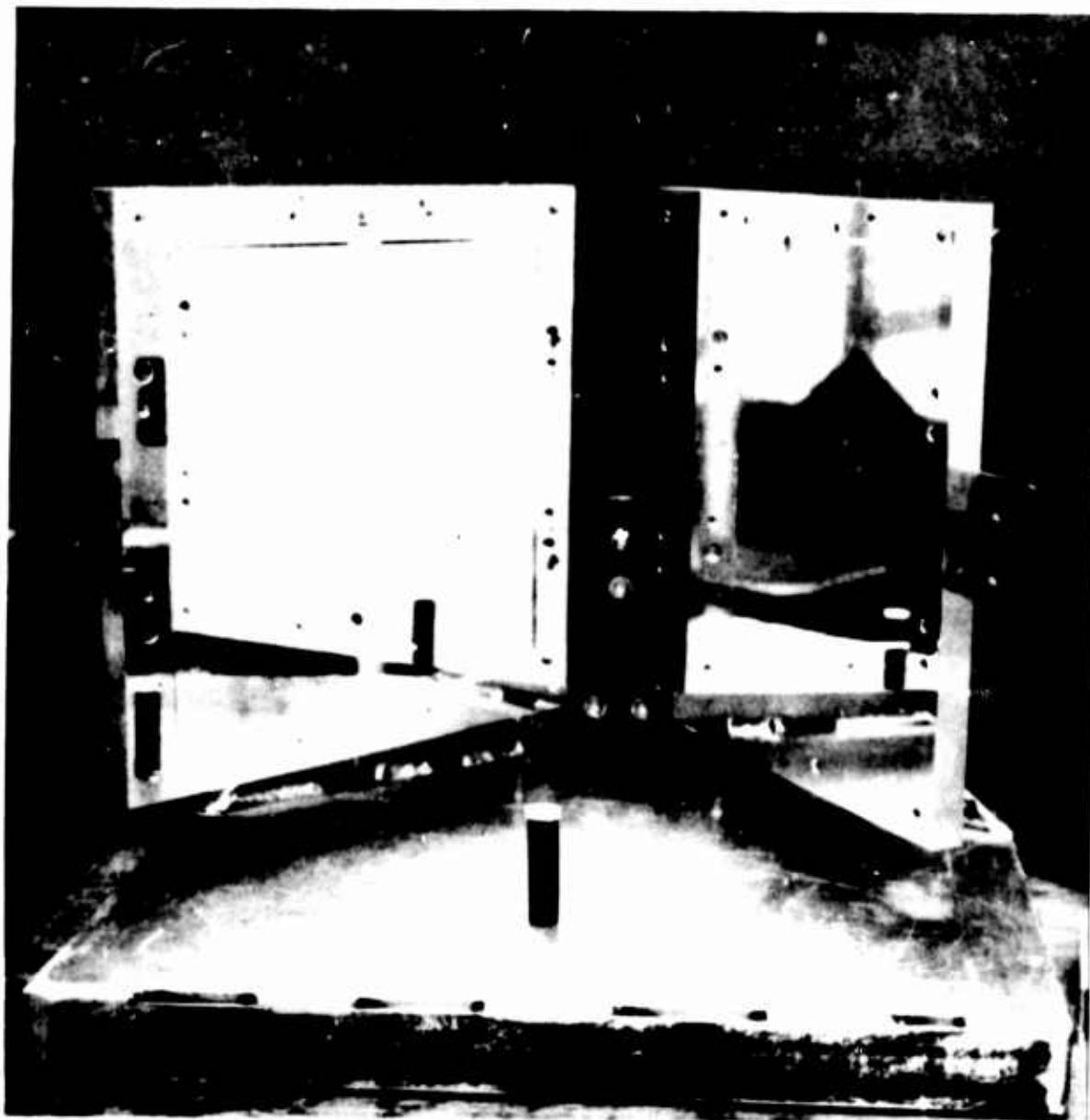
Figure 4. Sheet Mold; Dimensions of the Rubber
Sheet are: 12" x 12" x 0.1".
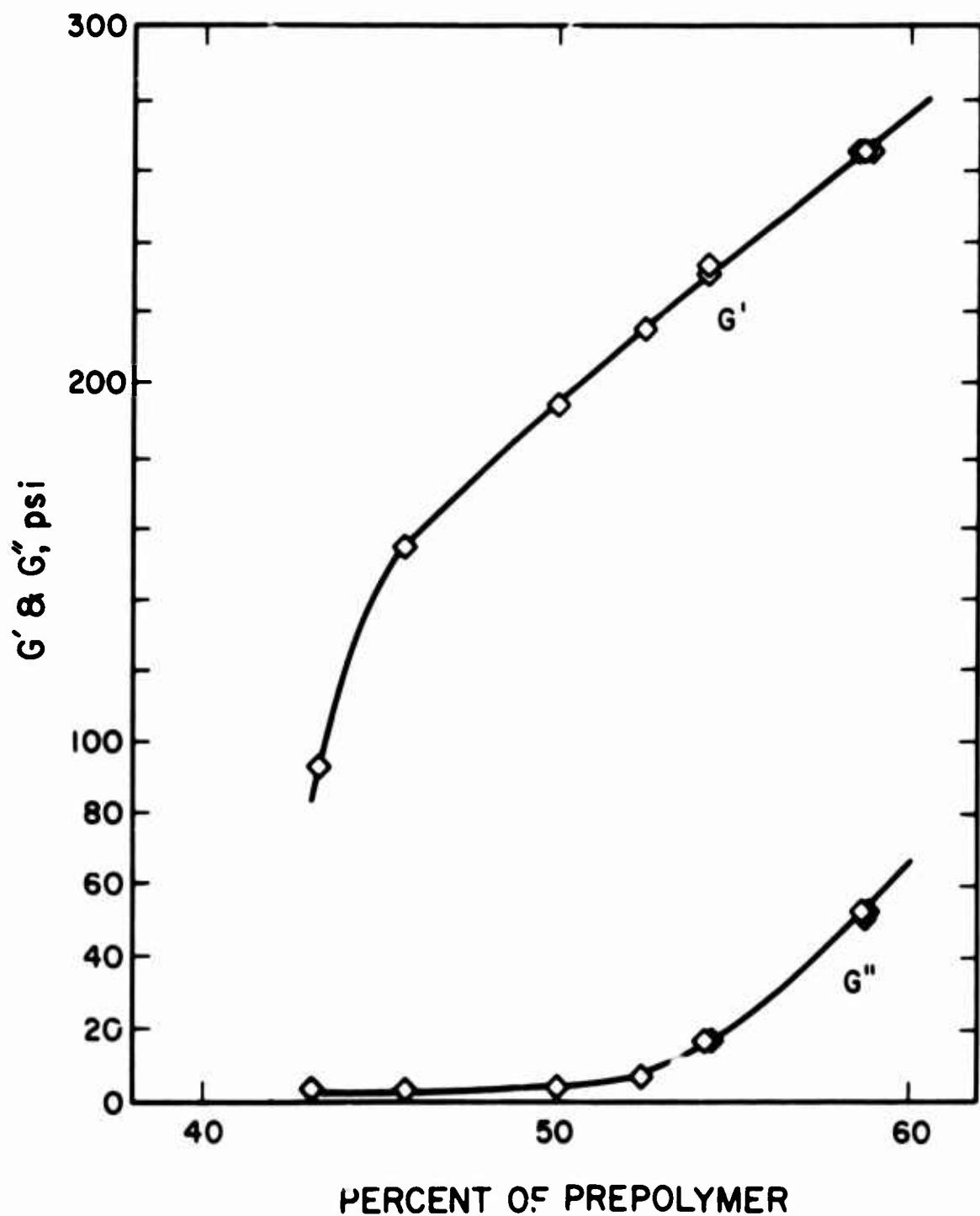
Figure 5. Complex Modulus at 20°C as a Function of
Prepolymer-Catalyst Composition.
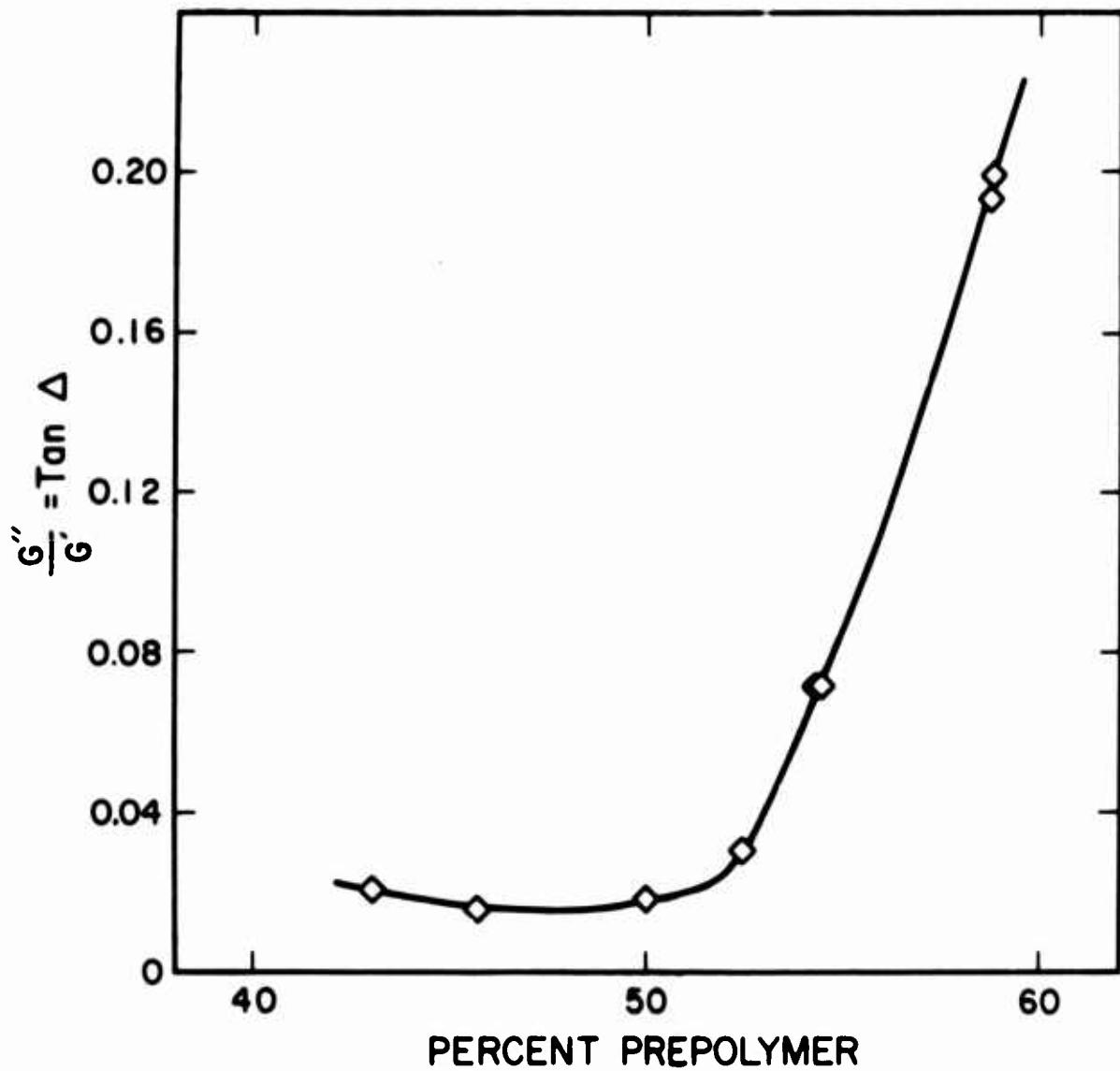
Figure 6. Loss Tangent for Data in Figure 5.
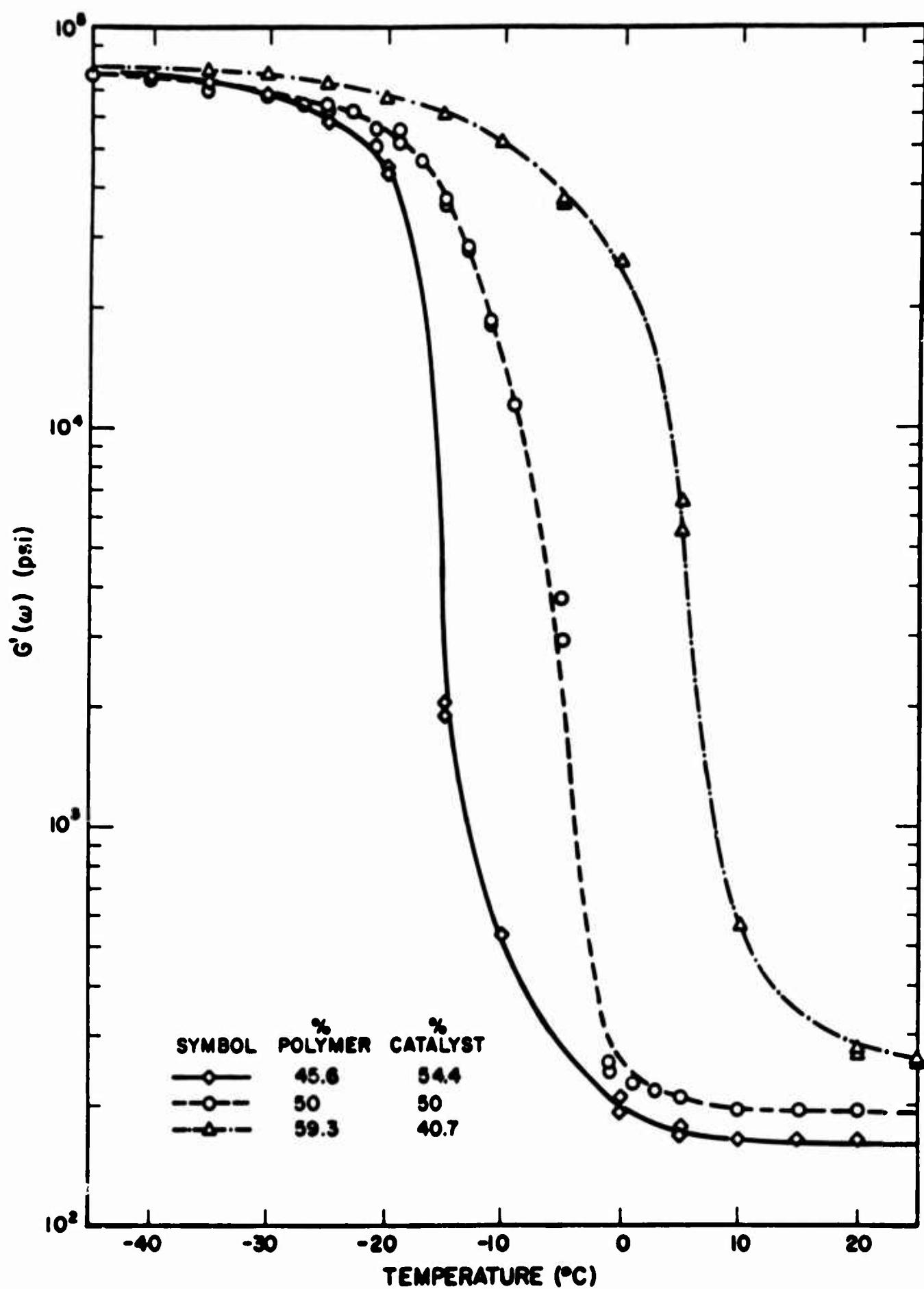
Figure 7.   Real Part of Complex Modulus as a Function of
Prepolymer-Catalyst Composition and Temperature.
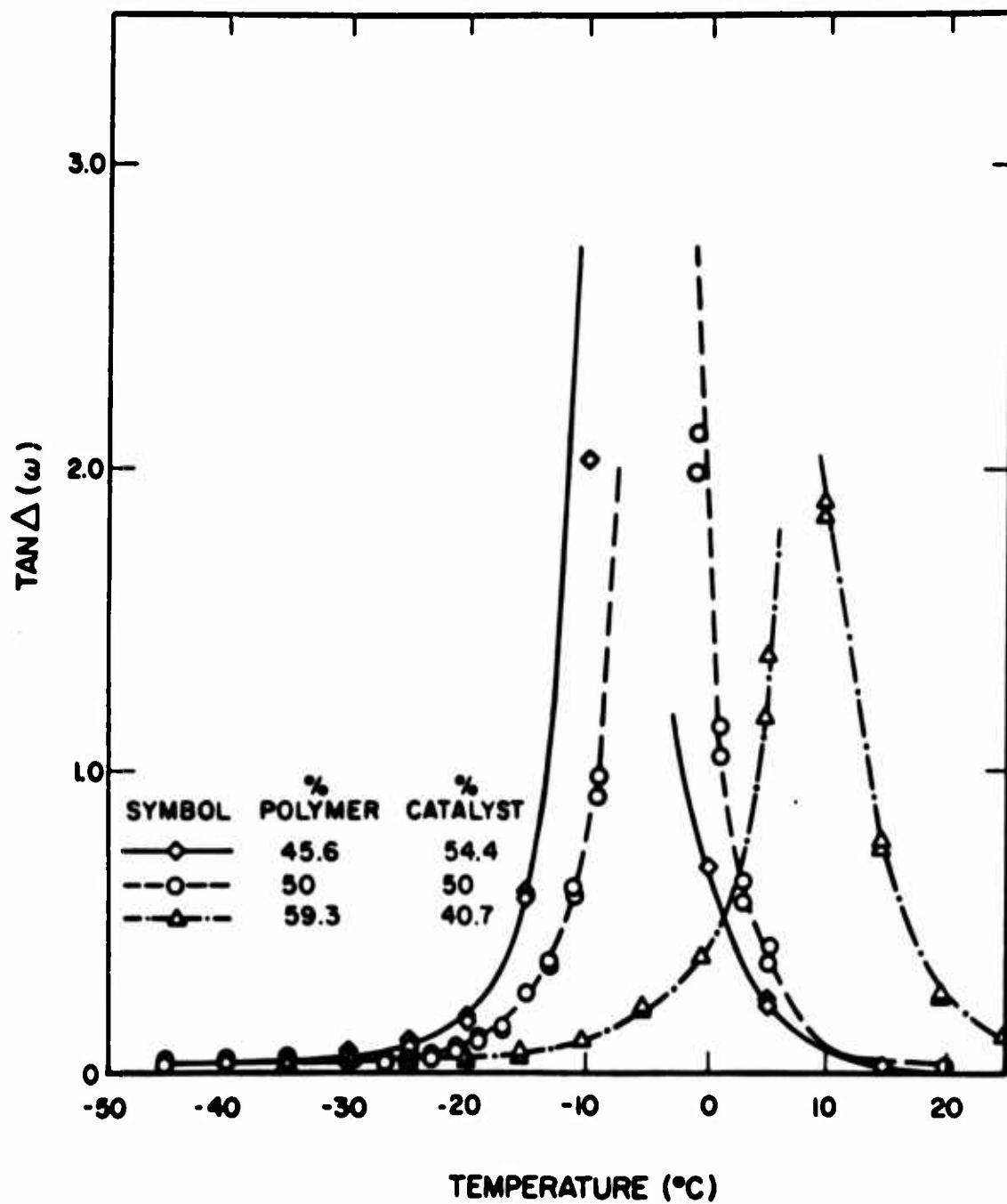
Figure 8. Loss-Tangent as a Function of Prepolymer-
Catalyst Composition and Temperature.
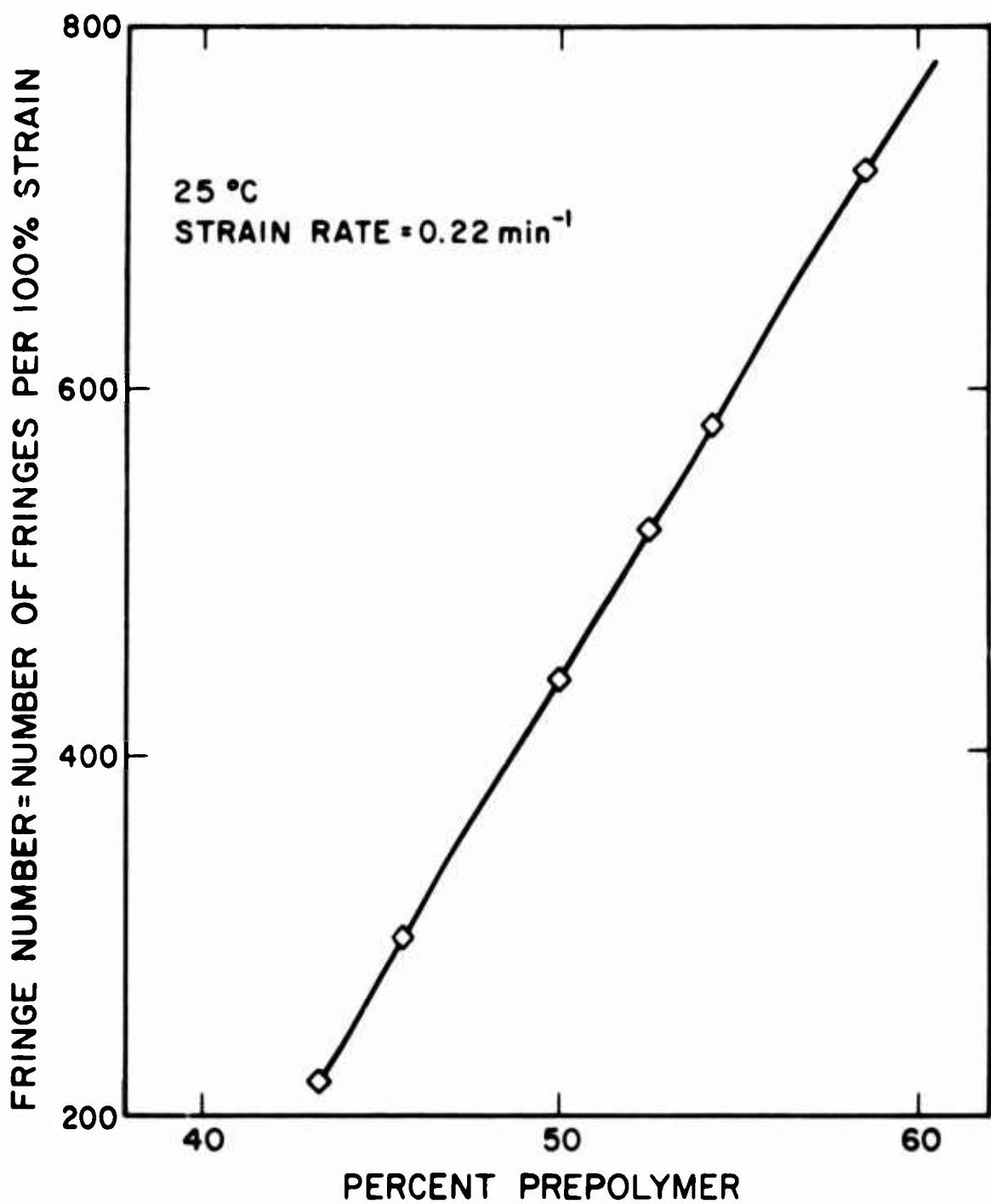
Figure 9. Strain-Optic Coefficient as a Function of
Prepolymer-Catalyst Composition at 20°C.
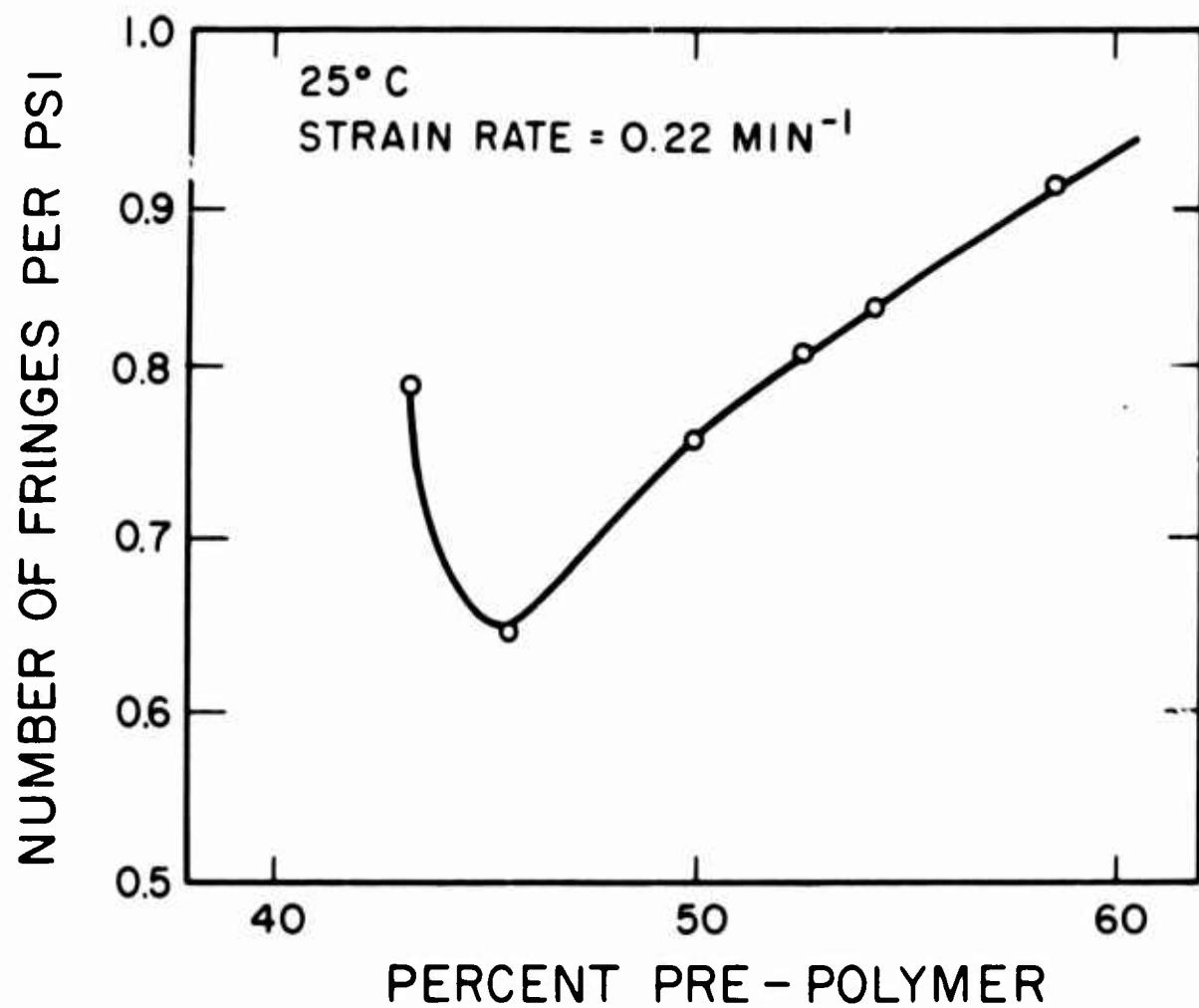
Figure 10. Stress-Optic Coefficient as a Function of Prepolymer-Catalyst Composition at 20°C.
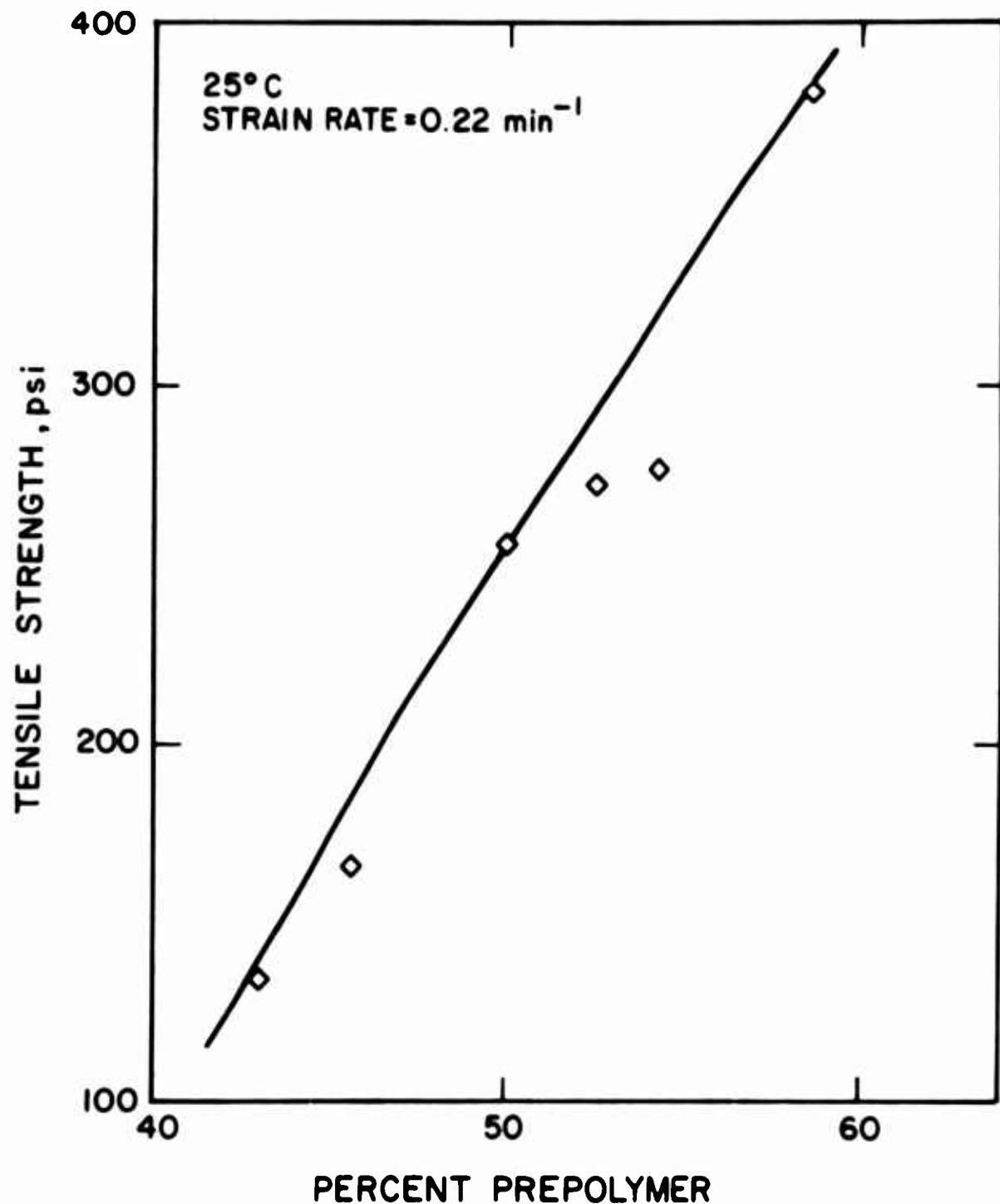
Figure 11. Uniaxial Tensile Strength as a Function of
Prepolymer-Catalyst Composition at 20°C.
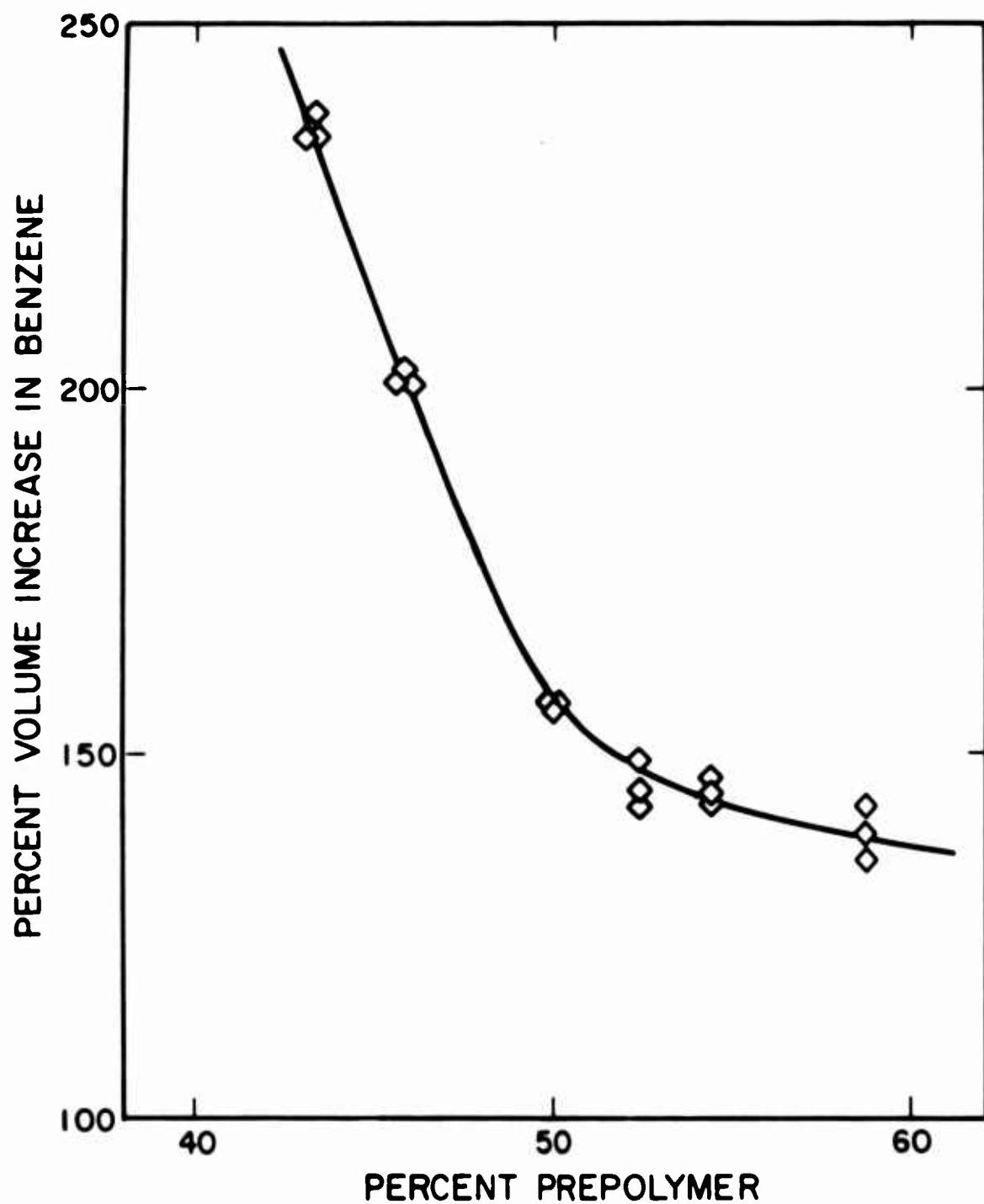
Figure 12.   Volume Change in Benzene after Two
Weeks at $25^{\circ}C$ as a Function of
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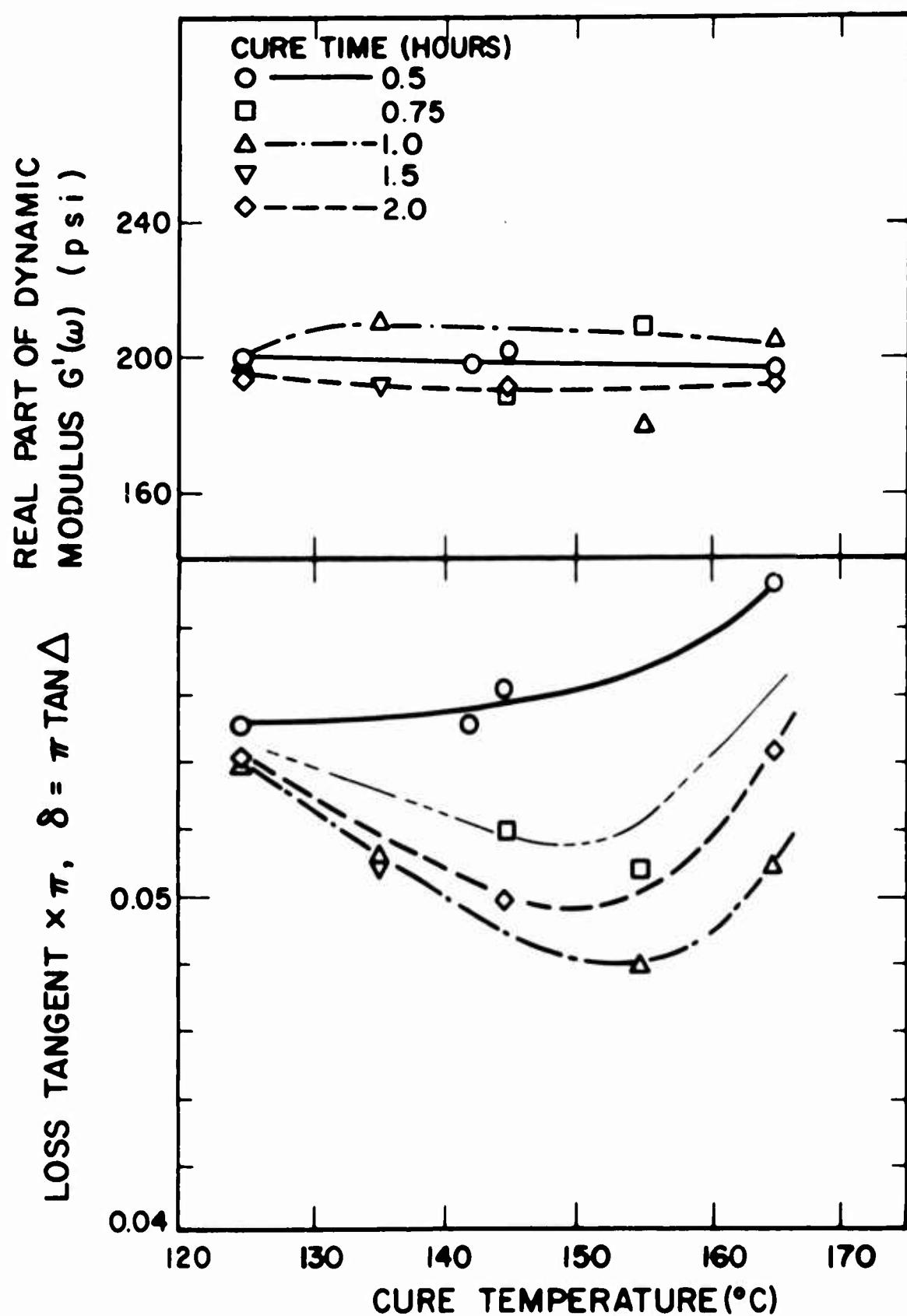
Figure 13. Effect of Cure Temperature on Real
Part of Complex Modulus and Loss
Tangent.
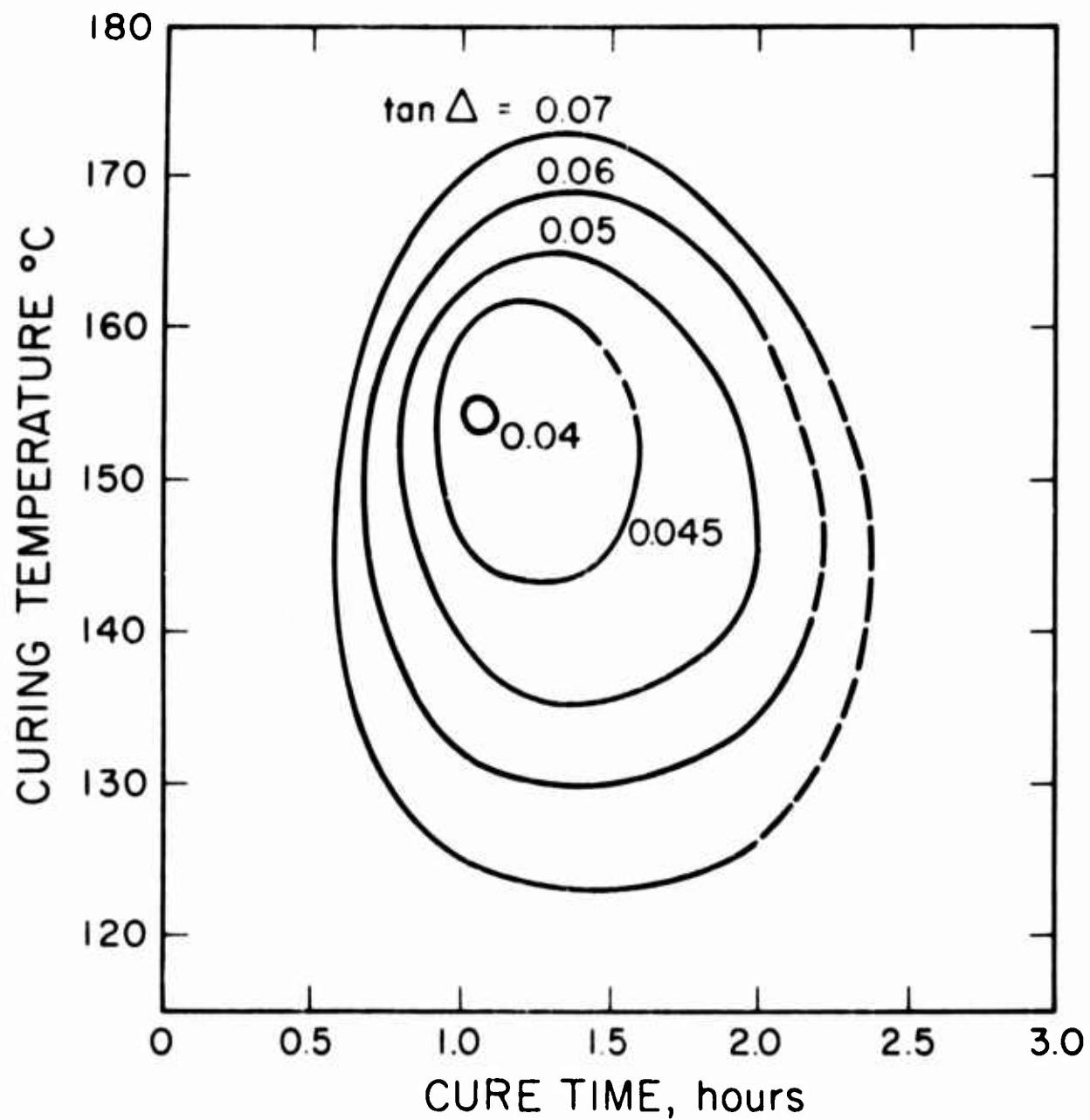
Figure 14. Contour Map of Loss Tangent as a Function
of Cure Time and Cure Temperature.
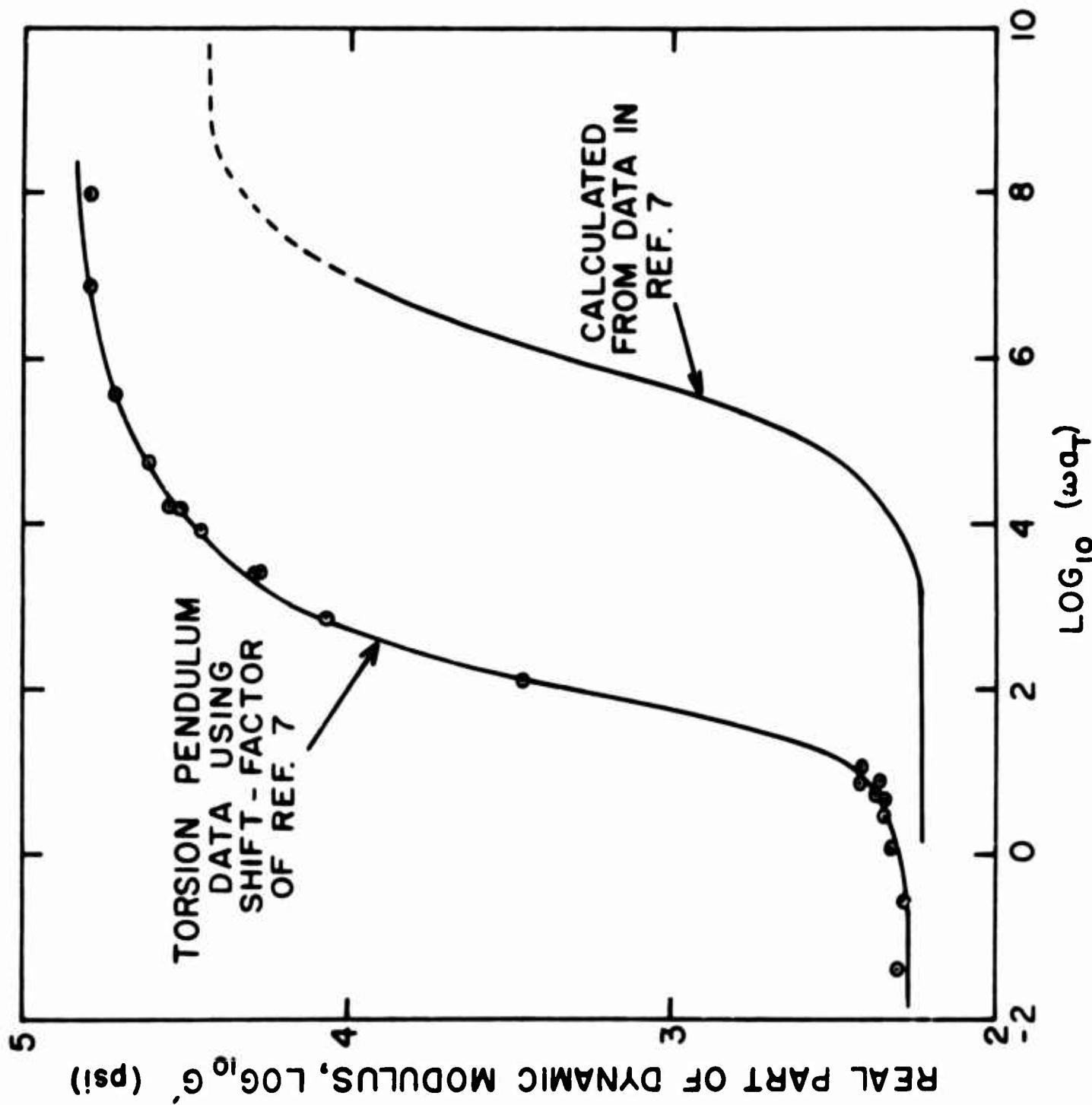
Figure 15. Comparison of Data from Reference 7 with Measurements Made with the Torsion Pendulum.
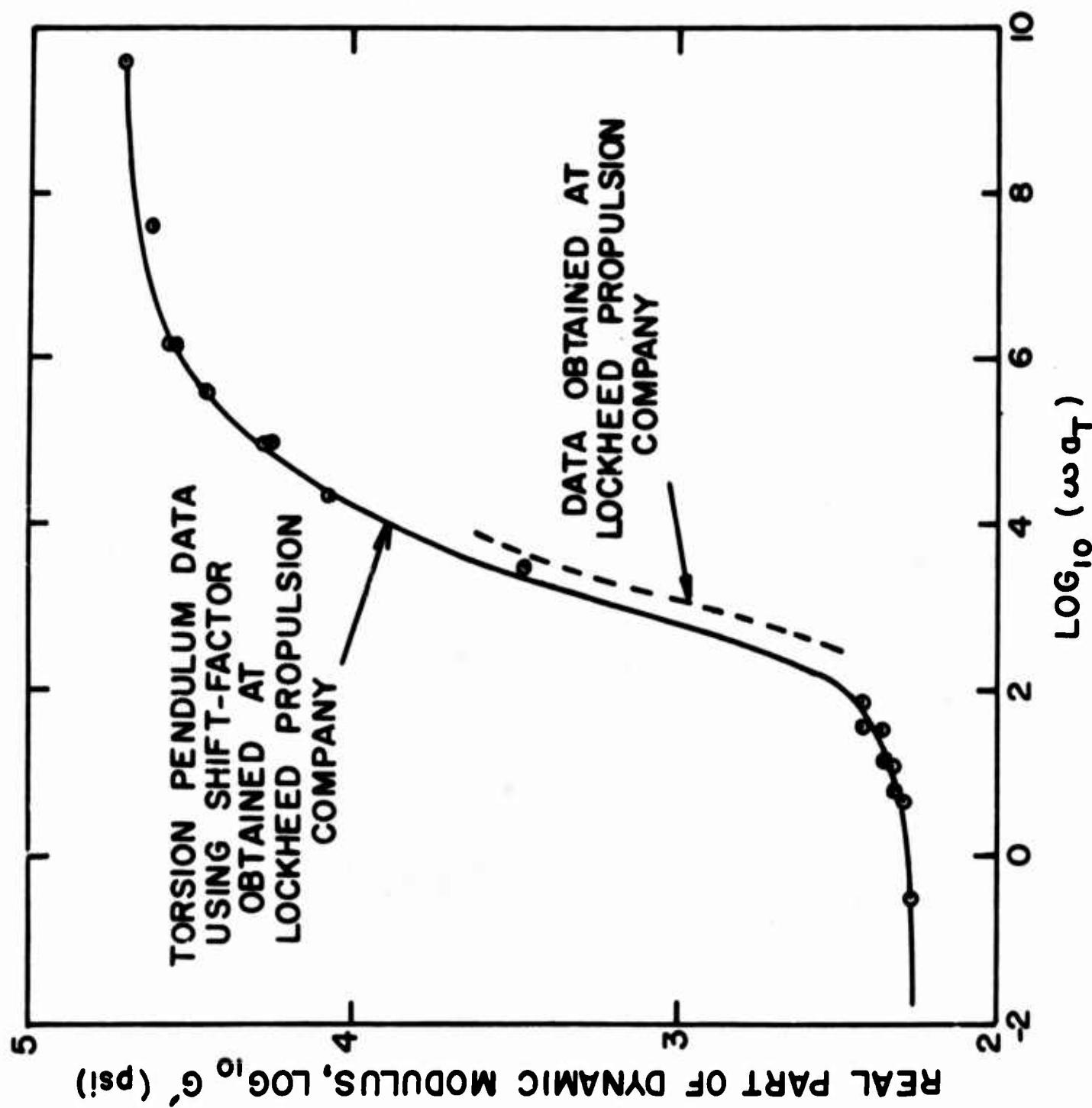
Figure 16. Comparison of Real Part of Complex Modulus as Obtained by Different Methods as Indicated. (See text for full details).
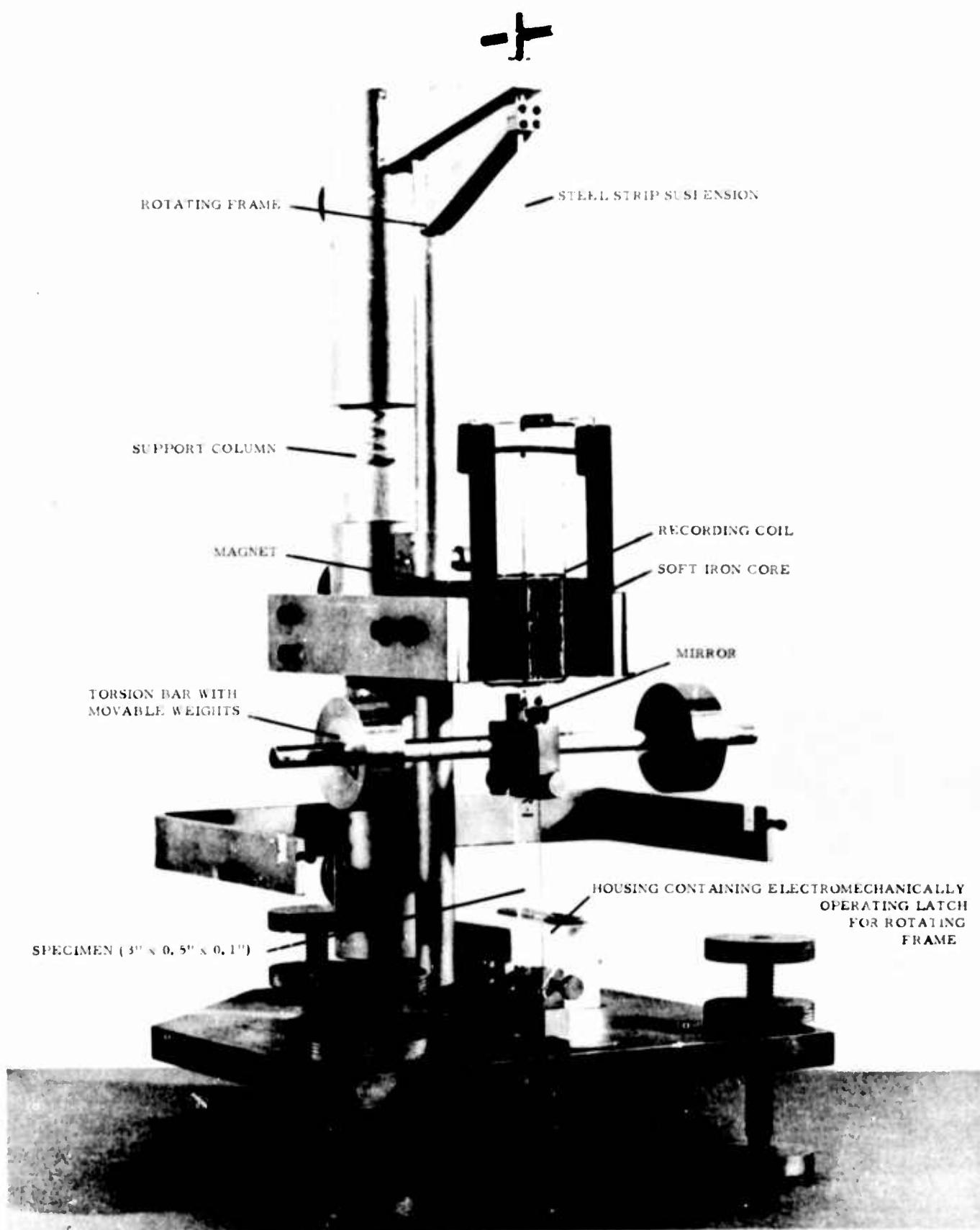
Figure 17.   Free Oscillation Torsion Pendulum.
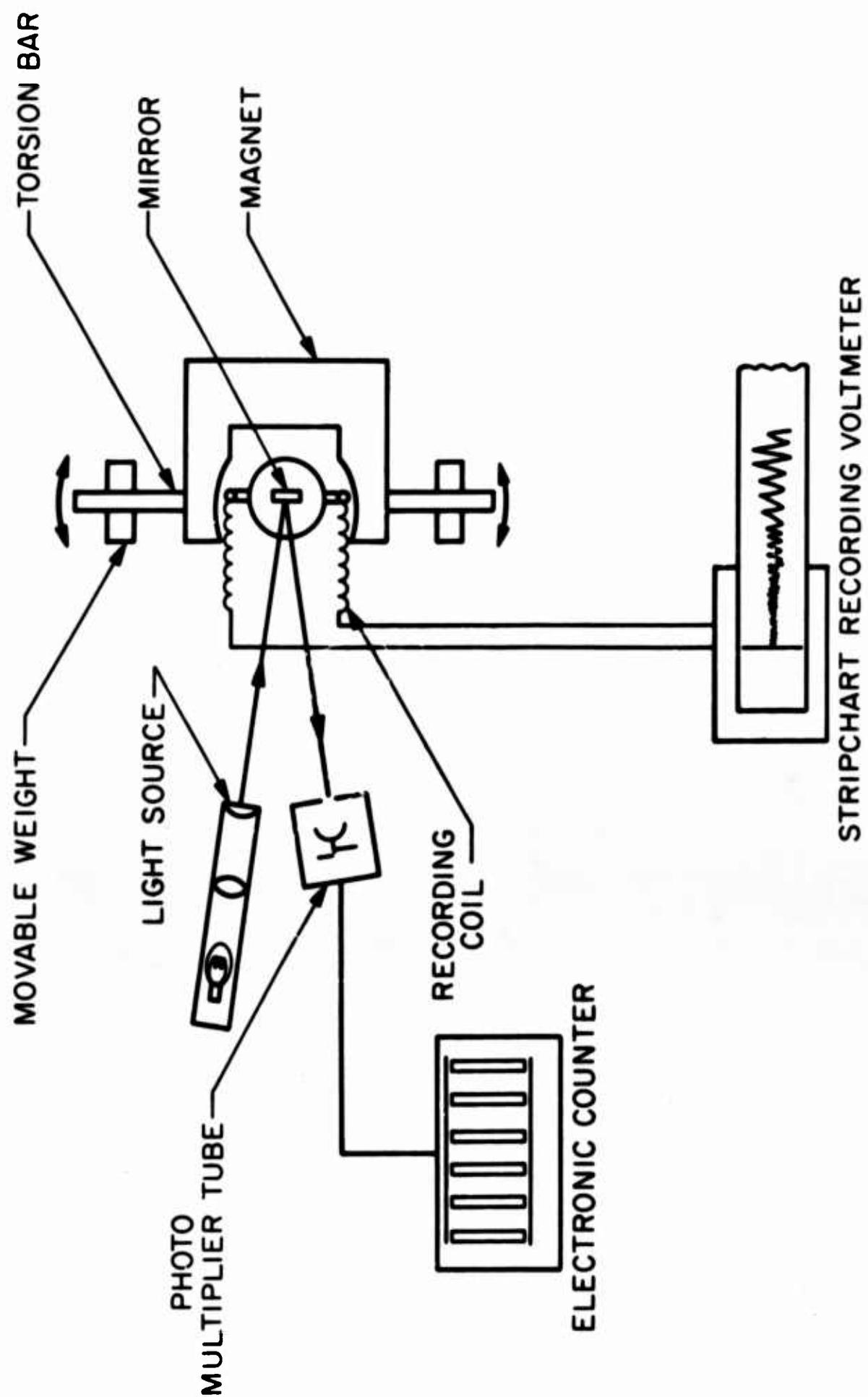
Figure 18. Diagramatic Arrangement of Torsion Pendulum and
Supporting Equipment.
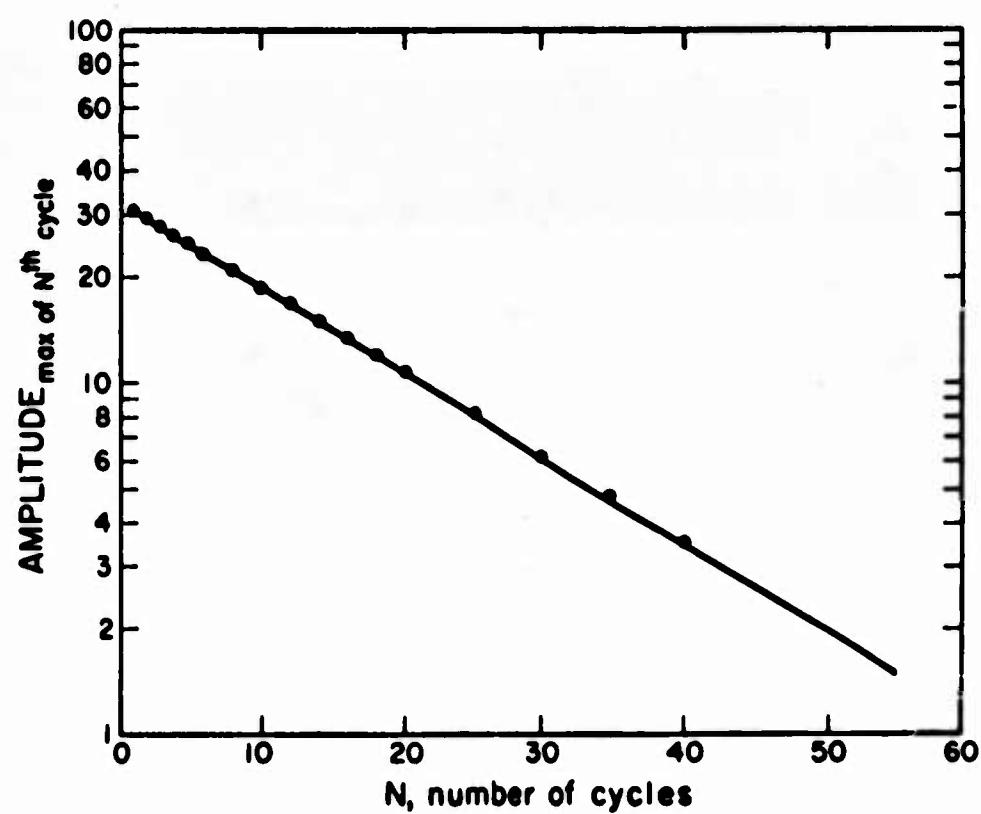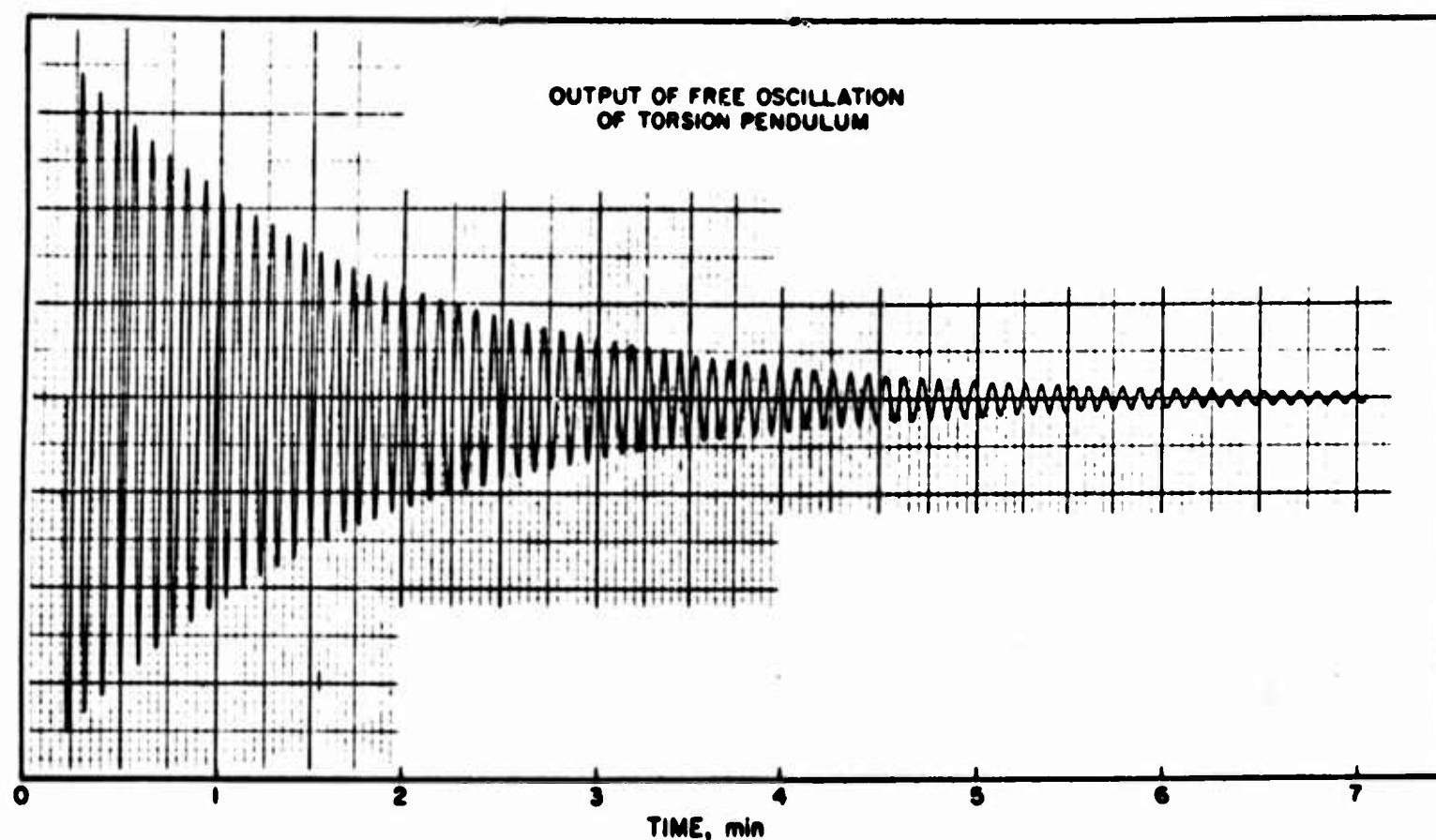
Figure 19. Typical Experimental Record Obtained with the Torsion Pendulum, and Semi-Logarithmic Plot of Velocity Maxima.